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THE INSTITUTE OF PETROLEUM

# To the Queen's Most Excellent Majesty

MAY IT PLEASE YOUR MAJESTY
on the occasion of the Coronation of Your Majesty, the President Council & members of
THE INSTITUTE OF PETROLEUM
present their humble duty to Your Majesty and offer on behalf of the Institute the assurance of their loyal affection and attachment to Your Throne and Person.
WE PRAY THAT ALMIGHTY GOD
may vouchsafe to Your Majesty health and strength to reign for many years in happiness over Your Peoples in the United Kingdom and beyond the seas.

PRESIDENT

HONORARY SECRETARY

June 2nd 1953

THE LOYAL ADDRESS TO HER MAJESTY
THE QUEEN

[To face inside cover ii.

# THE INSTITUTE OF PETROLEUM

AN Ordinary General Meeting of the Institute was held at 26 Portland Place, London, W.1, on 14 January 1953, Dr E. B. Evans, vice-president, in the Chair.

The General Secretary read the minutes of the preceding meeting, which were confirmed and signed, and the list of members elected since the previous meeting.

THE CHAIRMAN said: The paper this evening is to be delivered by one who is well known to many of us—Mr H. C. Rampton of the Anglo-Iranian Oil Company's Research Station at Sunbury. Mr Rampton has been interested in the problems of hydrocarbon type analysis for many years. He is in charge of a group dealing with methods of this kind at Sunbury, and has contributed very largely to our knowledge of the subject. He is interested in the subject from many points of view and has served on various Committees, such as the Hydrocarbon Analysis Panel of the Standardization Committee, and is secretary of the Hydrocarbon Chemistry Panel of the Hydrocarbon Research Group.

The following paper was then presented by H. C. Rampton:

## METHODS OF HYDROCARBON TYPE ANALYSIS

By H. C. RAMPTON *

SYNOPSIS

The preferred methods of hydrocarbon type analysis are presented, together with their scope and applicability, their limitations, and indications of the aims and trends of research either in progress or contemplated in the future. Compositions of naphtha and kerosine cuts from a variety of crude oils, determined by these methods, are included, and applications in the control of manufacture of special products instanced. Specimen analyses of cracked gasolines of various types are given for comparative purposes.

The influence of sulphur content on hydrocarbon type analysis in the gas oil boiling range is considered and assessments of gas oil composition made.

### INTRODUCTION

THE development of analytical methods by which the hydrocarbon type composition of petroleum products may be determined has received considerable attention in recent years. The first major application of such methods was seen in the last war, when the problem arose of supplying aviation gasolines of high anti-knock quality to satisfy the exacting needs of the newly developed high efficiency I.C. aircraft engines. The usefulness of such analyses was twofold, in that not only could estimates of yield be computed, but in most cases forecasts of actual performance quality in the engines could be made. It is now common practice to attempt to determine the hydrocarbon types in fractions from crude oil and

* Anglo-Iranian Oil Co. Ltd., Sunbury Research Station.

products arising from process operations, so that a knowledge of the chemical compositions of the feedstocks and products may be obtained and thereby an understanding gained of the chemical changes which occur in specific processes. The technical difficulties encountered in such analytical work are great, due to the highly involved and complex nature of the raw materials. In spite of this, considerable progress has been made towards the ultimate goal of analytical resolution of petroleum into individual hydrocarbons and non-hydrocarbon constituents. With the increasing employment of petroleum as a base stock for the manufacture of pure chemicals and the like, it is also of considerable importance to know the make-up of other than straight run products, *e.g.*, those resulting from processes such as cracking and reforming. The essential difference between straight run and cracked or reformed products is the presence in the latter of olefinic or unsaturated hydrocarbons, a factor which further complicates an already intricate problem.

The object of the present paper is to collect and present the preferred methods, together with their scope and applicability, their limitation and an indication of the aims and trends of research either in progress or contemplated in the future.

## Analysis of Saturated Products

The individual compounds present in straight run products boiling up to and including normal butane can be determined by accepted methods of gas analysis, based either on fractionation in packed columns of the Podbielniak type or the now widely used infra-red and mass spectroscopy, and will not be discussed further.

### *Gasolines* ($C_5$ *to* 225° *C E.P.*)

The hydrocarbons present in gasolines may be conventionally classified as paraffins, naphthenes, and aromatics. The paraffins represent the well defined saturated open chain structure hydrocarbons. The aromatics may be specified as cyclic hydrocarbons, as a predominant feature of their structure is the benzene ring with its characteristic resonating double bond unsaturation. The naphthenes have fully saturated carbon ring structures, and in the evidence to the contrary, straight run petroleum fractions are considered to contain five-membered and six-membered ring naphthenes only. The normal routine method of analysis aims at the estimation of the aromatics, naphthenes, and paraffins in cuts of specified boiling ranges, the cut points being selected in such a manner that individual hydrocarbons or groups of isomers are segregated as far as possible, so that the primary step in the procedure is that of fractional distillation, an art that has shown considerable progress. Various forms of ultra efficient column packings have been designed and used with great success in the laboratory, notably the glass and stainless steel helices of Fenske *et al*,[1] the spiral packings of Podbielniak,[2] the spiral screen of Lecky and Ewell,[3] the gauze cones of Stedman,[4] and the gauze cylinders due to Dixon.[5]

The essential conditions of the fractionation are that the efficiency of the column must be at least forty theoretical plates, the reflux ratio throughout not less than 40 : 1, and the dynamic hold-up of the column not greater than

5 per cent of the charge. The original gasoline is distilled under these conditions to give the following boiling range cuts :—

(i) 15° to 60° C;
(ii) 60° to 117° C (benzene + toluene);
(iii) 117° to 120° C;
(iv) 120° to 126° C (ethylbenzene);
(v) 126° to 140° C (ethylbenzene + isomeric xylenes);
(vi) 140° to 145° C (meta- and ortho-xylenes);
(vii) 145° to 150° C;
(viii) 150° to 175° C;
(ix) 175° to 200° C;
(x) 200° to 225° C.

Cuts (ii) to (vii) are examined by ultra-violet spectroscopic methods to determine the individual $C_6$, $C_7$, and $C_8$ aromatic hydrocarbons. Experience has shown that benzene is absent from the cut to 60° C and its examination is omitted. Knowledge of the percentage yields of the cuts enables a detailed distribution below 150° C to be calculated. Above 150° C, the total aromatic contents of cuts (viii) to (x) are estimated by chemical means, but if desired, individual $C_9$ and $C_{10}$ aromatics can be determined by spectroscopy if a number of narrower boiling range cuts are analysed from 150° to 200° C. In certain cases contents of naphthalene and methylnaphthalenes in the 200° to 225° C cut have also been estimated by ultra-violet spectroscopy.

The naphthene and paraffin hydrocarbons are obtained by examination of a second sample after removal of the aromatics, thereby avoiding the effect of abnormal vapour pressure relationships known to exist between aromatics and certain hydrocarbons. The removal of aromatics, without affecting the other hydrocarbons present, is accomplished by the convenient physical process of selective adsorption. The material is percolated (upward flow) through a column packed with 30 to 100-mesh silica gel, previously activated by heating at 380° to 400° C for 3 hr (each 100 g of gel adsorbs 8 g of aromatics) and the aromatic-free percolate of constant refractive index is segregated, equivalent to the naphthene–paraffin component. This percolate is fractionated using a column of efficiency not less than 100 theoretical plates, at a reflux ratio not less than 80 : 1, the dynamic

TABLE I

*Predominant Hydrocarbons Present in Naphthene plus Paraffin Component* ⟶ 120° *C*

| Boiling range, ° C | Paraffins | Naphthenes |
|---|---|---|
| 15 – 32·5 | *iso*Pentane | — |
| 32·5– 45 | Normal pentane | *cyclo*Pentane |
| 45 – 66 | *iso*Hexanes | *cyclo*Pentane |
| 66 – 75 | Normal hexane | Methyl*cyclo*pentane |
| 75 – 85 | Dimethylpentanes | *cyclo*Hexane |
| 85 – 95 | Methylhexanes | Dimethyl*cyclo*pentanes |
| 95 –109 | Normal heptane | Methyl*cyclo*hexane |
| 109 –120 | *iso*-Octanes | Trimethyl*cyclo*pentanes<br>Dimethyl*cyclo*hexanes |

hold-up being not greater than 5 per cent of the charge. Boiling point data on a weight basis are recorded and specific cuts segregated, the cut points being chosen with the deliberate intention of simplifying the subsequent analysis. The advantages gained may be best assessed by reference to Table I, wherein are listed the predominant hydrocarbons considered to be present in each cut.

Various routine methods for the estimation of the naphthene and paraffin contents of the selected cuts are available, the majority based on relationships between physical properties. The particular method chosen for routine work embodies specific refraction measurements, involving determination of density at 20° C (accuracy $\pm 0{\cdot}0001$ g/ml) and refractive index at 20° C—sodium D line (accuracy $\pm 0{\cdot}00005$). By linear interpolation, using mean values for the specific refractions of the naphthene and paraffins assumed to be present, the naphthene and paraffin contents of each cut are determined and expressed as weight percentages of the original gasoline. It is of interest to distinguish between and, as far as possible, estimate the two main types of naphthene hydrocarbons—namely, the five-membered ring, or *cyclo*pentane derivatives, and the six-membered ring, or *cyclo*hexane, derivatives. Below 95° C, this can be accomplished by reference to boiling point data and total naphthene contents of the cuts. Above 95° C, however, the cuts are processed over a platinum–charcoal catalyst under standard conditions, whereby dehydrogenation of the *cyclo*hexane type hydrocarbons occurs with the formation of aromatics.[6] Estimation of the latter enables the content of the six-membered ring naphthenes of each cut to be determined. It must be pointed out that geminal substituted six-membered ring compounds such as 1 : 1-dimethyl*cyclo*hexane, *i.e.*, those having two substituent groups attached to the same carbon atom, cannot be considered true hexahydro-aromatics, and hence do not dehydrogenate to aromatic hydrocarbons. For this reason, the results obtained by the dehydrogenation technique expressed in terms of five- and six-membered ring naphthenes may not represent the true composition, and it is preferred, therefore, to employ the terms " reactable " and " unreactable " instead, according as to whether they produce aromatics or not by this method of dehydrogenation.

The accuracy of the total naphthene estimation is limited by two considerations. First, isomers of the same molecular weight and type vary in specific refraction, and hence the mean values in the calculation may not coincide with those of the actual compounds present, although the error is probably not greater than $\pm 2$ per cent. Secondly, the presence of polycyclic naphthenes is possible in cuts boiling above 120° C, although it is generally accepted that the lowest boiling dicyclic naphthene present is decalin (b.p. 185·5° C).[7] Since polycyclic naphthenes are of vastly lower specific refraction, naphthene contents above 200° C would be better expressed as " average number of rings per molecule." The influence of this will be discussed further under Gas Oil.

Though the techniques outlined have such limitations as to accuracy and interpretation, nevertheless, the information gained has proved to be of the utmost value in the study of various feedstocks and products. Illustrative of the results obtained by routine analysis, typical naphtha compositions are given in Table II. More detailed information can be found by

TABLE II

*Hydrocarbon Type Composition—Naphthas to 225° C*

| Type | Boiling range, °C | Predominant hydrocarbons | A | | B | |
|---|---|---|---|---|---|---|
| Paraffins | IBP– 15 | Normal butane | — | | 1·19 | |
| | 15– 32·5 | *iso*Pentane | 2·02 | | 1·54 | |
| | 32·5– 45 | Normal pentane | 3·63 | | 1·68 | |
| | 45– 66 | *iso*Hexanes | 5·09 | | 2·97 | |
| | 66– 75 | Normal hexane | 4·78 | | 2·31 | |
| | 75– 85 | Dimethylpentanes | 0·92 | | 0·45 | |
| | 85– 95 | Methylhexanes | 3·86 | | 2·83 | |
| | 95–109 | Normal heptane | 5·83 | | 3·55 | |
| | 109–120 | *iso*-Octanes | 3·39 | | 3·00 | |
| | 120–130 | Normal octane | 5·68 | | 3·41 | |
| | 130–150 | *iso*- and Normal nonanes | 7·78 | | 4·72 | |
| | 150–175 | *iso*- and Normal decanes | 9·44 | | 6·49 | |
| | 175–200 | *iso*- and Normal undecanes | 7·76 | | 4·94 | |
| | 200–225 | *iso*- and Normal dodecanes | 7·06 | | 4·48 | |
| | Total | | 67·24 | | 43·56 | |
| Naphthenes | 32·5– 66 | *cyclo*Pentane | 0·02 | | 0·54 | |
| | 66– 75 | Methyl*cyclo*pentane | 0·64 | | 1·11 | |
| | 75– 85 | *cyclo*Hexane | 0·56 | | 1·29 | |
| | 85– 95 | Dimethyl*cyclo*pentanes | 0·87 | | 2·51 | |
| | 95–109 | Ethyl- and dimethyl*cyclo*-pentanes | 0·08 | 1·42 | 0·94 | 3·54 |
| | 95–109 | Methyl*cyclo*hexane | 1·34 | | 2·60 | |
| | 109–120 | Trimethyl*cyclo*pentanes | 0·33 | 0·97 | 1·24 | 2·03 |
| | 109–120 | Dimethyl*cyclo*hexanes | 0·64 | | 0·79 | |
| | 120–130 | Unreactable | 0·17 | 1·26 | 0·71 | 2·19 |
| | 120–130 | Reactable | 1·09 | | 1·48 | |
| | 130–150 | Unreactable | 1·01 | 2·52 | 2·84 | 4·84 |
| | 130–150 | Reactable | 1·51 | | 2·00 | |
| | 150–175 | Unreactable | 1·40 | 3·40 | 4·81 | 7·28 |
| | 150–175 | Reactable | 2·00 | | 2·47 | |
| | 175–200 | Unreactable | 2·90 | 4·66 | 4·12 | 6·26 |
| | 175–200 | Reactable | 1·76 | | 2·14 | |
| | 200–225 | Unreactable | 3·31 | 4·52 | 5·43 | 7·75 |
| | 200–225 | Reactable | 1·21 | | 2·32 | |
| | Total | Unreactable | 10·73 | 20·84 | 24·25 | 39·34 |
| | | Reactable | 10·11 | | 15·09 | |
| Aromatics | — | Benzene | 0·21 | | 0·59 | |
| | — | Toluene | 1·16 | | 2·24 | |
| | — | Ethylbenzene | 0·40 | | 0·61 | |
| | — | Paraxylene | 0·47 | | 0·58 | |
| | — | Metaxylene | 1·03 | | 1·43 | |
| | — | Orthoxylene | 0·76 | | 0·90 | |
| | 150–175 | $C_9H_{12}$ aromatics | 3·11 | | 4·57 | |
| | 175–200 | $C_{10}H_{14}$ aromatics | 2·52 | | 3·35 | |
| | 200–225 | $C_{11}H_{16}$ aromatics | 2·26 | | 2·83 | |
| | Total | | 11·92 | | 17·10 | |

analysing a large number of very narrow boiling range cuts by spectroscopic methods. In fact, in the case of materials of special type, it has been found possible to estimate the contents of all the individual hydrocarbons present. An example of such analysis and its application can be found in the case of blend stocks for aviation production during the war years

1939–45. It became evident that the then conventionally produced straight run blend stocks from Iranian crude would not be satisfactory, because of their low octane number and poor rich mixture rating.

It became essential to analyse for hydrocarbon type and to assess the way in which the various components affected the octane number and particularly the rich mixture performance. One result was the production, by superfractionation, from the $C_5$-100° C distillate, of "*iso*hexane cut" and "*iso*heptane cut."[7] From a knowledge of the true boiling point characteristics and the hydrocarbon type analyses of selected fractions of these products it was possible to express their constitution in terms of a limited number of groups of components. By assigning a blending factor to each group, it was possible to calculate the rich mixture performance of both blend stocks without recourse to an actual full scale engine test, and refineries could therefore produce specification materials without even possessing an engine on which to test them. A large saving in time, which was so essential at that particular war period, was also made, and a high percentage recovery of the valuable components was ensured, together with a minimum inclusion of low grade products.

*Kerosine and Gas Oil (225° to 350° C E.P.)*

The extension of the method used for determining the hydrocarbon type composition of gasolines to cover the higher boiling ranges of kerosines and gas oils up to 350° C is difficult for three main reasons. First, the number of isomers of each hydrocarbon type is extremely large, *e.g.*, there are over 10,000 possible paraffins of the formula $C_{16}H_{34}$, including hexadecane or cetane (b.p. 287·05° C). Secondly, the physical properties of the different groups of hydrocarbons are tending to approach each other, thus lessening the accuracy of differentiation between types. Thirdly, whereas in the gasoline range the sulphur content can be ignored, a sulphur content of 1·0 per cent by weight of a gas oil of molecular weight 200 corresponds to a sulphur compound content of 6 to 7 per cent by weight, assuming one sulphur atom present per molecule. Nevertheless, techniques have been developed which enable reasonably good assessments to be made of the make-up of materials in this boiling range.

The primary step in gas oil analysis is the isolation of the naphthene plus paraffin component by selective adsorption. A column, the length of which is at least sixty times the diameter, is packed with a weighed quantity of 30 to 100-mesh (BSS) silica gel, activated before use by roasting for 3 hr at 380° to 400° C. The charge of gas oil, corresponding to an adsorptive capacity of 5 g aromatics plus sulphur compounds per 100 g silica gel, is introduced into the column, followed by *iso*-octane (pure 2 : 2 : 4-trimethylpentane) eluant. An upward flow of 6 inches/hr through the adsorbent is maintained throughout. The liquid percolate from the top of the column is collected until the refractive index falls to that of pure eluant and no high boiling material remains as residue on distillation. The total percolate is transferred to a small solvent recovery still of *ca* three-plate efficiency and the bulk of the *iso*-octane eluant is removed, the last traces being stripped on a low hold-up vacuum column unit, leaving as a residue, the naphthene plus paraffin component. Percolation is continued, using

methanol as second eluant or desorbent, to desorb the aromatic plus thio component, the work-up being similar to that described for the naphthene plus paraffin component.

*Analysis of the Naphthene plus Paraffin Component*

The density ($d$) at 20° C is determined in a graduated double limb pyknometer (accuracy ±0·0001 g/ml) and the refractive index, $n_D^{20°C}$, measured on a Pulfrich refractometer (accuracy ±0·00005). The specific refraction is then calculated according to the formula :

$$\text{Specific refraction} = \frac{n^2 - 1}{n^2 + 2} \times \frac{1}{d}$$

Specific dispersion data and ultra-violet absorption measurements have confirmed that the naphthene plus paraffin component isolated by *iso*-octane elution as described is free from aromatic hydrocarbons and has a

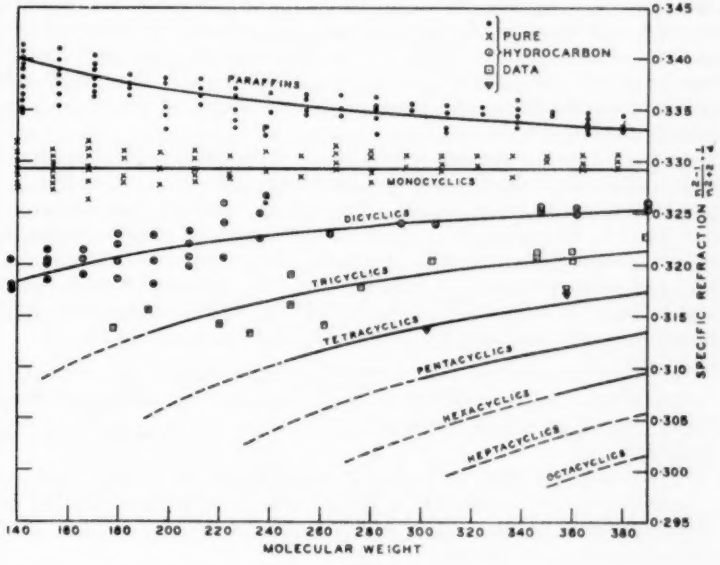


FIG 1

SPECIFIC REFRACTION–MOLECULAR WEIGHT RELATIONSHIPS FOR PARAFFINS AND NAPHTHENES

negligible sulphur content (usually of the order of 0·001 per cent by weight). Linear interpolation of the specific refraction value between the mean values for paraffins and monocyclic naphthenes of corresponding molecular weight enables a naphthene content to be calculated. The specific refraction/molecular weight relationships shown in Fig 1 have been derived from the atomic refractions of Eisenlohr [8] : C = 2·418, H = 1·100, and saturated five- and six-membered ring structures = 0·0, with atomic weights C = 12·01 and H = 1·008. It follows that the monocyclic

naphthenes ($C_nH_{2n}$) are of constant specific refraction, there being no exalting effect due to size of ring structure, *e.g.*, specific refraction of monocyclic naphthene of formula :

$$C_nH_{2n} = \frac{2{\cdot}418n + 1{\cdot}100{\cdot}2n}{12{\cdot}01n + 1{\cdot}008{\cdot}2n} = 0{\cdot}32925.$$

For dicyclic naphthenes ($C_nH_{2n-2}$), the specific refraction increases with rising molecular weight, the relationship being the same, whether the ring structure is five- or six-membered, fused or unfused, although, of course, the five-membered series exists at a lower molecular weight level than is possible with six-membered structures. The broken curves in Fig 1 illustrate this point. Similar considerations apply to the more complex series. The validity of these theoretical curves can be demonstrated only by comparison with the values for pure hydrocarbons known to exist in the boiling range under consideration. Added to the curves of Fig 1 are such values for synthetic pure paraffins and naphthenes as are considered to be the best obtainable at the present juncture.[9] The agreement between these values and the theoretical mean, despite the spread of the former, is reasonable, considering the relatively small number of synthesized hydrocarbons when compared with the enormous possibilities. The spread of the actual determined values, of course, is due to effects of the overall configuration of the molecule.

Interpolation by the specific refraction method involves the assumption that the molecular weights of the naphthenes and of the paraffins in a specific boiling range are identical. Any error caused by this assumption is considered to be negligible. There is one aspect of paraffin/naphthene analysis, however, which must be discussed, that of the mode of reporting. Considering point *P* on Fig 1, the analysis of a sample of such specific refraction may be expressed in a variety of ways, depending on the assumptions made regarding the particular homologues present :—

1. If only paraffins and monocyclic naphthenes are present the composition can be calculated as 50 per cent paraffins and 50 per cent naphthenes, equivalent to an average of 0·5 naphthene rings/molecule.
2. If only paraffins and dicyclic naphthenes are present the composition can be calculated as 75 per cent paraffins and 25 per cent naphthenes, although it is still equivalent to an average of 0·5 naphthene rings/molecule.

Again, a sample represented by point *Q* (Fig 1) could similarly be expressed in a number of ways, depending on the assumption made as to the types of naphthene present. It is therefore the practice to obtain analyses in the form " *x* naphthene rings per molecule " in the first instance and subsequently to make assumptions regarding the nature of the naphthenes.

This method of differentiating naphthenes and paraffins by specific refraction measurements has an inherent inaccuracy, because the analyst is forced to take as his basis the mean values for the naphthene and paraffin hydrocarbon. The same criticism can be levelled at all methods based on correlation of physical properties. The use of determined carbon and hydrogen contents would enable C/H ratios to be used instead of specific

refraction, since the same type of curve would be obtained. The added advantage of this method would be that all isomers of the same type and the same molecular weight would have identical ratios. Normal techniques in the determination of carbon and hydrogen do not give the required accuracy (better than ±0·01 per cent), and the method therefore has not been used extensively up to the present. Recent investigation at Sunbury, however, has indicated that the method of Wear and Quiram [10] is capable of yielding carbon and hydrogen contents with an accuracy of ±0·01 per cent, and it may be possible to develop a scheme of analysis which would prove superior to that employing specific refraction. The final analysis, however, will still have to be quoted with the provisos, "average number of naphthene rings per molecule" or "naphthenes calculated as monocyclics."

Further development of this analysis will depend on the separation of the paraffins from the naphthenes, and subsequently the subdivision of the naphthenes into their component classes. The first separation is being attempted at Sunbury, using long, narrow columns packed with silica gel adsorbent. The results obtained for the naphthene plus paraffin component of a Middle East crude cut (b.p. 220° to 340° C) are given in Table II. These data were obtained by percolating 150 g of sample through 3000 g of 30 to 100-mesh silica contained in two columns in series, each 26 feet in length, the first of 1·0 inch I.D. and the second of 0·5 inch I.D. The adsorptogram technique was adopted, the desorbing liquid being 2-ethylhexanol, chosen on account of its density, viscosity, and immiscibility characteristics. The degree of separation, while not completely satisfactory, is nevertheless

TABLE III

*Separation of Naphthenes and Paraffins—Analyses of Blends of Fractions from Selective Adsorption on Silica Gel*

| Blend of fractions | Yield on original, wt % | Density at 20° C, g/ml | Ref. index, $n_D^{20°C}$ | Specific refraction, $\frac{n^2-1}{n^2+2}\cdot\frac{1}{d}$ | Naphthene rings per molecule | Analyses by *n–d–M* method * | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | | % $C_N$ | % $C_R$ | $R_N$ | $R_T$ |
| 1– 36 | 18·49 | 0·7824 | 1·43788 | 0·33543 | 0·17 | 10·1 | 11·0 | 0·28 | 0·30 |
| 37– 42 | 4·33 | 0·7853 | 1·43845 | 0·33457 | 0·29 | 13·9 | 13·9 | 0·41 | 0·42 |
| 43– 50 | 6·00 | 0·7872 | 1·43915 | 0·33424 | 0·29 | 15·1 | 15·2 | 0·45 | 0·46 |
| 51– 59 | 6·51 | 0·7888 | 1·44022 | 0·33425 | 0·33 | 15·7 | 16·2 | 0·47 | 0·49 |
| 60– 65 | 4·11 | 0·7922 | 1·44075 | 0·33316 | 0·48 | 20·6 | 20·5 | 0·59 | 0·59 |
| 66– 71 | 3·90 | 0·7929 | 1·44132 | 0·33325 | 0·46 | 20·6 | 20·5 | 0·59 | 0·59 |
| 72– 77 | 4·04 | 0·7945 | 1·44222 | 0·33317 | 0·48 | 21·3 | 21·3 | 0·61 | 0·61 |
| 78– 83 | 3·96 | 0·7971 | 1·44308 | 0·33263 | 0·55 | 23·5 | 23·5 | 0·65 | 0·66 |
| 84– 89 | 4·04 | 0·8001 | 1·44454 | 0·33233 | 0·59 | 25·8 | 25·8 | 0·69 | 0·70 |
| 90– 97 | 4·65 | 0·8002 | 1·44456 | 0·33230 | 0·59 | 25·8 | 25·8 | 0·69 | 0·70 |
| 98–103 | 3·82 | 0·8045 | 1·44589 | 0·33140 | 0·71 | 31·2 | 30·5 | 0·82 | 0·82 |
| 104–109 | 3·74 | 0·8067 | 1·44650 | 0·33087 | 0·78 | 32·6 | 31·8 | 0·89 | 0·89 |
| 110–116 | 3·29 | 0·8100 | 1·44758 | 0·33021 | 0·87 | 36·8 | 35·8 | 0·95 | 0·95 |
| 117–122 | 4·49 | 0·8154 | 1·44975 | 0·32942 | 0·97 | 40·1 | 39·0 | 1·09 | 1·09 |
| 123–128 | 3·75 | 0·8195 | 1·45148 | 0·32886 | 1·05 | 42·8 | 41·9 | 1·18 | 1·18 |
| 129–134 | 4·41 | 0·8248 | 1·45293 | 0·32764 | 1·22 | 49·0 | 47·0 | 1·30 | 1·28 |
| 135–140 | 4·79 | 0·8331 | 1·45586 | 0·32619 | 1·41 | 52·1 | 50·1 | 1·46 | 1·42 |
| 141–146 | 3·82 | 0·8381 | 1·45806 | 0·32562 | 1·49 | 54·1 | 52·0 | 1·55 | 1·53 |
| 147–150 | 2·54 | 0·8417 | 1·45990 | 0·32533 | 1·53 | 54·5 | 53·3 | 1·55 | 1·54 |
| 151–154 | 2·77 | 0·8438 | 1·46041 | 0·32483 | 1·59 | 56·8 | 54·9 | 1·63 | 1·61 |
| 155–159 | 2·55 | 0·8463 | 1·46141 | 0·32447 | 1·64 | 58·0 | 56·0 | 1·67 | 1·65 |
| Summation | 100·00 | — | — | — | 0·68 | — | — | 0·79 | — |

* % $C_N$ = Percentage of total carbon atoms in naphthene rings.
% $C_R$ = Percentage of total carbon atoms in all rings.
$R_N$ = Average number of naphthene rings/molecule.
$R_T$ = Average number of all rings/molecule.

encouraging, and it is hoped to continue this study. As a matter of interest, the specific refraction data are compared, also in Table III, with results obtained by the use of the *n–d–M* method published by van Nes and van Westen.[11] Since the molecular weight of the cut examined—206—is on the lower limit of applicability of the *n–d–M* method, the agreement can be considered reasonable.

The urea adduction process has been tried, on an analytical basis, to ascertain the extent of the normal paraffin content, but without much success. The adducts formed with kerosine and gas oil cuts do not contain the normal paraffins to the exclusion of all other hydrocarbons, as much as 11 per cent naphthenes and 5 per cent aromatics being present on occasion in the hydrocarbon yield on decomposition.

*Analysis of the Aromatics plus Thio Component*

In the early chromatographic studies with silica gel and petroleum distillates it was usual to observe the development of colour on the adsorbent throughout the aromatic plus thio component zone, and particularly at the interface of this zone with the desorbent. Recovery of the aromatic plus thio component invariably led to the production of a brown liquid, the optical properties of which could not be determined. Investigation of this point disclosed that the chief source of trouble was the free acidity of the gel. This acidity was determined as *ca* 2 g $H_2SO_4$ per 100 g gel, and therefore, with a charge of 30 g gas oil feed, the selective adsorption process was equivalent to a 7 per cent by weight acid wash. Hence, the dark colour in fact was due to the formation of " acid tar." In addition, any iron sulphate present in the gel dissolved in the methanol to give a brownish solution. A special neutral grade silica gel of low iron content (*ca* 0·02 per cent weight Fe) was obtained from the suppliers. This material proved satisfactory, and has been the standard grade at Sunbury over the last three years. In use, very little colour developed, a pale straw tint only being observed at interface between the methanol desorbent and the aromatic plus thio component, a fact which enabled determinations of optical properties to be carried out.

The assumption that one atom of sulphur per molecule of sulphur compound is present is made and the percentage thio component calculated from the molecular weight and sulphur content, the aromatic component being obtained by difference. The results are converted to the basis—original sample ≡ 100 per cent by calculation, knowing the yield of aromatic plus thio component obtained from the selective adsorption process. The lack of information and data concerning aromatic hydrocarbons and sulphur compounds in the boiling range above 200° C has prevented extension of the analysis by any scheme based on additive physical properties alone, and it is probable that the exalting effect of aromatic and sulphur containing nuclei would, in any case, render interpretation of the results difficult, since it varies from structure to structure. Typical hydrocarbon type compositions of distillates boiling in the range 225° to 350° C, determined by the accepted method are given in Table IV. It will be seen that sulphur compound contents of the order of 13 per cent weight are encountered. Although the assumption made regarding the number of sulphur atoms per molecule is inadequate as a permanent basis of analysis, the

calculated thio components of such boiling range material are deemed sufficient reason for distrusting published methods, which, almost without exception, ignore the presence of sulphur compounds. A true assessment of any method of analysis is dependent upon the quantitative separation of aromatic hydrocarbons from sulphur compounds.

Partial separation has indeed been achieved at Sunbury during silica gel adsorption studies. A charge of 8315 g of 340° C end point gas oil of Middle East origin was percolated through 40 kg silica gel contained in four 12-foot columns connected in series in the order : one 2-inch, two 4-inch, and finally one 2-inch diameter. *iso*-Octane (2 : 2 : 4-trimethylpentane) was used to elute the naphthene plus paraffin component as a single percolate, from which the eluant was removed by distillation. The four columns were desorbed separately with pure benzene to yield the aromatic plus thio components. Finally, the four columns were reconnected in series and desorbed with methanol to yield a small quantity of asphaltic material. The material desorbed by benzene from the first column had a sulpher content of 12·60 per cent weight, which, assuming 1 S atom per molecule, corresponds to a concentration of sulphur compounds of 75 per cent, but equivalent to barely 20 per cent of the total sulphur present,

TABLE IV

*Hydrocarbon Type Compositions of Gas Oil Cuts—225° to 350° C*

| Sample | Boiling range, °C | Hydrocarbon types | | | |
|---|---|---|---|---|---|
| | | Aromatic, % wt | Naphthene, % wt | Paraffin, % wt | Sulphur compounds, % wt |
| A | 225–250 | 19·8 | 50·2 | 28·5 | 1·5 |
| | 250–275 | 21·4 | 49·5 | 25·1 | 4·0 |
| | 275–300 | 21·4 | 51·9 | 21·0 | 5·7 |
| | 300–325 | 19·7 | 49·1 | 23·7 | 7·5 |
| | 325–350 | 24·0 | 44·5 | 20·5 | 11·0 |
| B | 225–250 | 23·7 | 32·8 | 41·2 | 1·3 |
| | 250–275 | 22·2 | 36·1 | 37·8 | 3·9 |
| | 275–300 | 25·2 | 32·7 | 34·2 | 7·9 |
| | 300–325 | 23·3 | 32·0 | 33·9 | 10·8 |
| | 325–350 | 21·6 | 35·2 | 29·7 | 13·5 |

the remainder being distributed between the material desorbed from the other columns. Clear cut and complete separation of sulphur compounds in concentrations approaching 100 per cent and in 100 per cent yields will prove difficult, and it is improbable that the method will be of value for routine type analysis.

Since bromine number addition was known to occur with sulphur compounds but not with benzene homologues, it was thought that " bromine number " estimation would prove a useful guide to the nature of the aromatic plus thio component. The Francis bromine number method used in the gasoline range is inadequate for coloured samples, and an alternative was sought. The final choice was one based on an electrometric technique described by Dubois and Skoog [12] subsequently adopted by the ASTM as a

standard method. It gives theoretical bromine numbers for pure unsaturated hydrocarbons, but no bromine addition is indicated with paraffins, naphthenes, and benzene homologues. Mercaptans, sulphides, cyclic sulphides, and disulphides all react appreciably with bromine. Unfortunately, the extent of reaction not only varies from type to type but also from member to member of the same type (see later). Some evidence also exists for the addition of bromine to polycyclic aromatics. The inferences that can be drawn from bromine numbers, therefore, are contradictory and of little use in analysis.

An alternative mode of attack that has been attempted at Sunbury is to treat the original kerosine or gas oil with reagents reputed to extract the sulphur compounds without affecting the hydrocarbons present, prior to isolating the naphthene plus paraffin and aromatic components by selective adsorption. Such a material is boron trifluoride hydrate,[13] but preliminary work has indicated only partial success. The most efficacious technique consisted of passing $BF_3$ gas through a mixture of gas oil and $BF_3H_2O$ liquid. The results are shown in Table V, wherein it is seen that a

TABLE V

*Boron Trifluoride Hydrate Treatment of Gas Oil*

| Volume % $BF_3H_2O$ | Refractive index of raffinate, $n_D^{20°C}$ | Sulphur content of raffinate, % wt |
|---|---|---|
| 0 | 1·46754 | 0·84 |
| 1 | 1·46605 | 0·48 |
| 5 | 1·46371 | 0·22 |
| 10 | 1·46296 | 0·19 |
| 50 | 1·46292 | 0·19 |

77 per cent desulphurization can be achieved. The removal of the remaining 23 per cent by this reagent, however, was not found possible. The physical properties of the naphthene plus paraffin components of the original and desulphurized gas oil do not show any significant difference, from which it is inferred that the $BF_3$ reagent does not attack these hydrocarbons. Selective adsorption analysis of the treated and untreated gas oil yields a percentage of aromatic plus thio component in agreement with the degree of desulphurization, thus indicating that this reagent does not attack the aromatic hydrocarbons.

It was considered that a valuable guide to the type of sulphur compound present would be obtained if it were possible to hydrogenate selectively the sulphur compounds without affecting the hydrocarbons.[14] The analysis of the breakdown products would then enable limits to be set on the quantities of various sulphur compound types and the actual aromatic content determined. Using a similar plant to that used for routine hydrogenation of olefines (see later) a crude gas oil cut was processed under the conditions :

| | |
|---|---|
| Catalyst . . . . | cobalt molybdate on alumina type. |
| Feed rate . . . | 1·00 v/v/hour. |
| Pressure . . . . | 250 p.s.i.g. |
| Hydrogen feed . . . | ≡ 3575 CF/B. |

The temperature of the catalyst bed was maintained during four separate runs at 540° F, 620° F, 700° F, and 780° F. The results, including selective adsorption analysis data, are given in Table VI. Comparison of the physical properties of the naphthene plus paraffin components of the products of hydrogenation suggested that the dehydrogenation of naphthenes to aromatics does not occur if the reaction temperature is limited to 700° F. Equally, no hydrogenation of aromatics to naphthenes takes place below 700° F, since no significant increases in refractive index were observed up to this temperature of operation. It was also demonstrated in a separate experiment that the naphthene plus paraffin component could be processed at 700° F without change. It was realized, of course, that selective desulphurization of a whole range gas oil did not achieve all that was to be desired from an analytical standpoint, inasmuch as some of the hydrocarbons formed as breakdown products would boil within the original boiling range. A study of the data available for boiling points of sulphur compounds elicited the fact that the minimum difference between any sulphur compound and its hydrocarbon breakdown product would exceed 30° C. It was suggested, therefore, that by restricting the

TABLE VI

*Gas Oil—Physical Properties and Selective Adsorption Analyses of Feed and Desulphurized Products*

| | Before selective adsorption | | | | | Naphthene + paraffin component | | Aromatic + thio component | |
|---|---|---|---|---|---|---|---|---|---|
| | Density at 20° C, g/ml | Refractive index, $n_D^{20°C}$ | Sulphur content, % wt | Naphthene + paraffin, % wt | Aromatic + thio component, % wt | Density at 20° C, g/ml | Refractive index, $n_D^{20°C}$ | Density at 20° C, g/ml | Refractive index, $n_D^{20°C}$ |
| Gas oil feed . . | 0·8399 | 1·4687 | 0·87 | 73·1 | 26·9 | 0·8056 | 1·4463 | 0·9538 | 1·5442 |
| After desulphurization: | | | | | | | | | |
| At 540° F . . | 0·8347 | 1·4660 | 0·22 | 75·4 | 24·6 | 0·8065 | 1·4465 | 0·9499 | 1·5339 |
| At 620° F . . | 0·8321 | 1·4647 | 0·11 | 75·3 | 24·7 | 0·8061 | 1·4463 | 0·9352 | 1·5241 |
| At 700° F . . | 0·8326 | 1·4648 | 0·01 | 75·7 | 24·3 | 0·8056 | 1·4461 | 0·9209 | 1·5250 |
| At 780° F . . | 0·8318 | 1·4645 | <0·01 | 71·5 | 28·5 | 0·8023 | 1·4448 | 0·9259 | 1·5301 |

boiling range of the cut examined to 20° C it would be possible to isolate the breakdown products by simple distillation to the original I.B.P. of the cut. This procedure would not only permit an analysis of the hydrocarbons formed on desulphurization but would also make possible the examination of the original aromatic hydrocarbons free from sulphur compounds. Such an experiment has been performed, using a 250° to 270° C boiling range cut prepared by fractionation on a twenty-plate vacuum column unit at a reflux ratio of 20 : 1, charge to hold-up ratio being 50 : 1.

A quantity of 5 litres of the 250° to 270° C cut (sulphur = 0·92 per cent by weight) was processed at 700° F reactor temperature and 250 p.s.i.g., at an average space velocity of 1·00 v/v/hr, with plant modifications to allow gas recycle. The total products were collected in evacuated

Calor gas containers, overall weight balances being made and every precaution taken to prevent loss, in view of the expected yield of breakdown products, $C_1$ and upwards, of only 4·51 per cent by weight ≡ 172 g. The product was transferred from the Calor gas bottle to the twenty-plate vacuum column unit via a side arm attached to the flask, methanol cooling at −25° C being applied to the condensers during charging. Any incondensible gas passed to a gas-holder and was analysed subsequently (Table VII). The distillation was continued to an overhead temperature of

TABLE VII

*Selective Desulphurization of 250° to 270° C Cut—Yields of Breakdown Products*

| Fraction no. | Boiling range, °C | % wt of original cut | Density at 20° C g/ml | Refractive index, $n_D^{20°C}$ |
|---|---|---|---|---|
| 1 (Gas) | Methane | 0·01 | — | — |
| | Ethane | 0·03 | — | — |
| | Propane | 0·05 | — | — |
| | Butanes | 0·05 | — | — |
| | Pentanes | 0·02 | — | — |
| 2 | 24·2– 45·0 | 0·06 | — | — |
| 3 | 45·0– 75·0 | 0·17 | 0·69484 | 1·38946 |
| 4 | 75·0– 95·0 | 0·21 | 0·73000 | 1·40300 |
| 5 | 95·0–109·0 | 0·17 | 0·74850 | 1·41649 |
| 6 | 109·0–125·0 | 0·20 | 0·75241 | 1·41855 |
| 7 | 125·0–140·0 | 0·23 | 0·77434 | 1·43289 |
| 8 | 140·0–150·0 | 0·11 | 0·80288 | 1·43788 |
| 9 | 150·0–166·8 | 0·22 | 0·80620 | 1·45144 |
| 10 | 166·8–175·0 | 0·20 | 0·82869 | 1·46723 |
| 11 | 175·0–183·7 | 0·22 | 0·83741 | 1·47222 |
| 12 | 183·7–188·5 | 0·23 | 0·83739 | 1·47218 |
| 13 | 188·5–191·8 | 0·22 | 0·84017 | 1·47464 |
| 14 | 191·8–193·3 | 0·23 | 0·84088 | 1·47608 |
| 15 | 193·3–194·5 | 0·22 | 0·84224 | 1·47631 |
| 16 | 194·5–196·2 | 0·22 | 0·84144 | 1·47596 |
| 17 | 196·2–198·4 | 0·23 | 0·83939 | 1·47472 |
| 18 | 198·4–200·0 | 0·14 | 0·83877 | 1·47378 |
| 19 | 200·0–202·0 | 0·25 | 0·84396 | 1·47355 |
| 20 | 202·0–204·0 | 0·23 | 0·84204 | 1·47425 |
| 21 | 204·0–208·0 | 0·26 | 0·84018 | 1·47210 |
| 22 | 208·0–210·0 | 0·24 | 0·82372 | 1·46656 |
| 23 | 210·0–213·0 | 0·22 | 0·82486 | 1·46474 |
| 24 | 213·0–216·0 | 0·22 | 0·81796 | 1·45630 |
| 25 | 216·0–221·0 | 0·23 | 0·81073 | 1·45353 |
| 26 | 221·0–225·0 | 0·24 | 0·82026 | 1·45858 |
| 27 | 225·0–231·0 | 0·24 | 0·84378 | 1·47203 |
| 28 | 231·0–236·0 | 0·26 | 0·86324 | 1·48412 |
| 29 | 236·0–239·0 | 0·25 | 0·87124 | 1·48821 |
| 30 | 239·0–243·0 | 0·25 | 0·87662 | 1·48496 |
| 31 | 243·0–245·0 | 0·24 | 0·84965 | 1·48450 |
| 32 | 245·0–247·0 | 0·24 | 0·83992 | 1·46960 |
| 33 | 247·0–247·0 | 0·25 | 0·83193 | 1·46545 |
| 34 | 247·0–247·0 | 0·24 | 0·82738 | 1·46336 |
| 35 | 247·0–250·0 | 0·23 | 0·82586 | 1·46268 |

250° C. The small quantity of breakdown products necessitated a refractionation of the I.B.P.-250° C material on a forty-plate column for more precise measurement. T.B.P. data and physical properties of fractions are given in Table VII and Fig 2. The separation between breakdown

products and original components is not so clear cut as could be desired. The sulphur content of the original gas oil cut (0·92 per cent by weight) corresponds to a content of sulphur compounds of 5·43 per cent by weight assuming an average of 1 sulphur atom per molecule. A maximum yield of breakdown products of *ca* 4·51 per cent by weight is indicated therefore, or in actual weight only 172 g. The location of this yield is shown in Fig 2 by line *AB*.

The analysis of the fractions boiling below 210° C proved difficult. Attempts were made to apply selective adsorption techniques but the

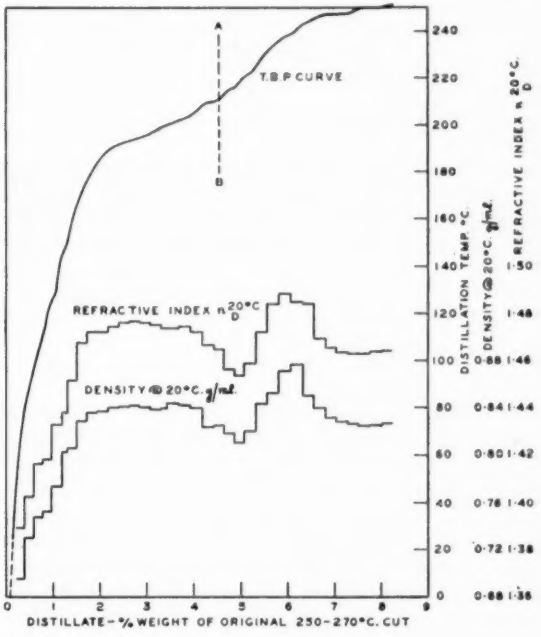


FIG 2

DESULPHURIZED MIDDLE EAST GAS OIL 250° TO 270° C CUT. TBP CURVE AND PROPERTIES OF FRACTIONS

small quantities available did not permit a high degree of accuracy. From the data, however, some general inferences could be drawn. Up to 95° C, no appreciable amount of benzene could be detected, and the material is predominantly paraffinic. Above 95° C, the aromatic content rises slowly to *ca* 50 per cent at 200° to 210° C. The non-aromatic constituents above 100° C are increasingly naphthenic, and indeed, above 160° C appear to consist essentially of the dicyclic naphthenes, refractive indices of 1·458 to 1·464 ($n_D^{20°C}$) being encountered. The corresponding values for monocyclic naphthenes and paraffins boiling between 160° and 210° C are 1·433 to 1·447 and 1·410 to 1·425 respectively, while the dicyclic naphthenes cover the range 1·45 to 1·48. These dicyclic naphthenes could be derived

from homologues of sulphur compounds of all or any of the following types :—

(I) S–H decalin thiol

(II) S–H hydrindane thiol

(III) S–H bicyclo-octane thiol

(IV) S–R thia-alkyldecalin

(V) S–R thia-alkylhydrindane

(VI) S–R thia-alkylbicyclo-octane

(VII) 1 : 4-endothiadecalin

Since mercaptan contents of gas oil fractions are known to be extremely low, the possibility of the presence of types (I), (II), and (III) is remote. Tricyclic sulphur compounds having the sulphur atom in the ring could also give rise to dicyclic naphthenes on breakdown by selective hydrogenation, viz.:—

Information regarding the physical properties of such compounds is sparse, but, by analogy with the corresponding hydrocarbons, it is considered that they would boil above the boiling range of the sample examined here. The approximate composition of the total breakdown products was calculated and found to be 29 per cent by weight aromatics, 14 per cent by weight paraffins, and 57 per cent by weight naphthenes. The conclusion, therefore, is that the sulphur compounds are predominantly dicyclic naphthenes having thia-alkyl substituents or a sulphur bridge in the nucleus. This conclusion is supported by the small yield of low-boiling hydrocarbons.

The material boiling above 250° C was taken to be representative of the original constituents of the cut, since the conditions were such that the hydrocarbons were not affected. The naphthene plus paraffin component isolated by the normal selective adsorption technique compared closely with the original naphthenes plus paraffins in physical properties (Table VIII). The date of Table IX obtained by examining successive boiling range fractions indicate that the average number of naphthene rings per molecule varies between 0·54 and 1·08.

The corresponding aromatic component was also examined (Table X). It must be emphasized that this product was equivalent to the aromatic hydrocarbons present in the original gas oil cut, and isolated for the first time virtually free from sulphur compounds. Previously, it had not been possible to examine such aromatics without interference from sulphur compounds. Data embracing the physical properties of aromatic type hydrocarbons in the gas oil range are very meagre, but nevertheless, by

TABLE VIII

*Hydrocarbon Type Analyses of 250° to 270° C Boiling Range Cut ex Gas Oil—Original and Desulphurized Material*

| | Original cut | Desulphurized and breakdown products removed |
|---|---|---|
| Sulphur content, % wt | 0·92 | 0·02 |
| *Hydrocarbon type composition :* | | |
| Naphthenes, % wt | 53·3 | 54·4 |
| Paraffins, % wt | 19·6 | 20·6 |
| Aromatics, % wt | 21·7 | 24·9 |
| Sulphur compounds, % wt | 5·4 | 0·1 |
| *Naphthene plus paraffin component :* | | |
| Yield, % wt | 72·9 | 75·0 |
| Density at 20° C, g/ml | 0·8012 | 0·8002 |
| Refractive index at 20° C : | | |
| $n_D$ | 1·44426 | 1·44329 |
| $n_F$ | 1·44940 | 1·44868 |
| $n_C$ | 1·44173 | 1·44108 |
| Specific refraction $\frac{n^2-1}{n^2+2}\cdot\frac{1}{d}$ | 0·33144 | 0·33148 |
| Specific dispersion $(n_F - n_C) \times 10^4/d$ | 95·7 | 95·0 |
| Paraffin content, % wt | 26·9 | 27·4 |
| Naphthene content, % wt | 73·1 | 72·6 |
| *Aromatic plus thio component :* | | |
| Yield, % wt | 27·1 | 25·0 |
| Density at 20° C, g/ml | 0·9499 | 0·9346 |
| Refractive index at 20° C : | | |
| $n_D$ | 1·54573 | 1·53827 |
| $n_F$ | 1·55413 | 1·55067 |
| $n_C$ | 1·53604 | 1·53327 |
| Specific refraction $\frac{n^2-1}{n^2+2}\cdot\frac{1}{d}$ | 0·33322 | 0·33391 |
| Specific dispersion $(n_F - n_C) \times 10^4/d$ | 192·2 | 185·7 |

TABLE IX

*Desulphurized 250° to 270° C Cut ex Gas Oil Naphthene Plus Paraffin Component >250° C*

| Boiling range of fraction, °C | Yield, wt % | Density at 20° C, g/ml | Refractive index at 20° C | | | Specific dispersion $(n_F - n_C)\times 10^4/d$ | Specific refraction, $\frac{n^2+2}{n^2-1}\cdot\frac{1}{d}$ | Average no. of naphthene rings/mol |
|---|---|---|---|---|---|---|---|---|
| | | | $n_D$ | $n_F$ | $n_C$ | | | |
| 249·5–250·0 | 2·4 | 0·7969 | 1·44206 | 1·44776 | 1·43989 | 98·8 | 0·33205 | 0·64 |
| 250·0–251·5 | 10·5 | 0·7960 | 1·44161 | 1·44719 | 1·43944 | 97·4 | 0·33212 | 0·63 |
| 251·5–253·0 | 15·8 | 0·7916 | 1·44124 | 1·44657 | 1·43924 | 92·2 | 0·33248 | 0·59 |
| 253·0–257·0 | 15·8 | 0·7967 | 1·44242 | 1·44797 | 1·44033 | 95·9 | 0·33237 | 0·60 |
| 257·0–262·0 | 16·1 | 0·8061 | 1·44585 | 1·45132 | 1·44369 | 94·7 | 0·33070 | 0·81 |
| 262·0–264·5 | 15·9 | 0·8020 | 1·44467 | 1·45000 | 1·44228 | 96·3 | 0·33165 | 0·69 |
| 264·5–265·0 | 10·6 | 0·7975 | 1·44296 | 1·44826 | 1·44054 | 96·8 | 0·33239 | 0·60 |
| 265·0–269·0 | 9·3 | 0·7908 | 1·44042 | 1·44578 | 1·43822 | 95·6 | 0·33354 | 0·45 |
| 269·0–270·0 | 3·6 | 0·8125 | 1·44634 | — | — | — | 0·32841 | 1·08 |

assuming the presence of three classes, viz., benzene, tetralin, and naphthalene derivatives, an approximate idea of the composition of distillate fractions was formed from density/refractive index relationships (Table X). The overall composition is seen to be 36 per cent by weight monocyclic, 33 per cent by weight naphthalenes, and 31 per cent by weight tetralins. These calculations can be considered as approximate only, but the agreement between the calculated and determined specific dispersion values

suggest that they are not far from the true compositions. The presence of tetralin derivatives was confirmed by ultra-violet spectroscopic examination, but no estimate of the amounts could be given owing to the masking

TABLE X

*Desulphurized 250° to 270° C Cut from Gas Oil—Aromatic plus Thio Component*

| Boiling range, °C | Yield, wt % | Density at 20° C, g/ml | Refractive index at 20° C | | | Specific dispersion $(n_F - n_C) \times 10^4/d$ | Monocyclic aromatics, % wt | Dicyclic aromatics, % wt | Tetralins, % wt | Specific dispersion $(n_F - n_C) \times 10^4/d$ (calc.) |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | $n_D$ | $n_F$ | $n_C$ | | | | | |
| 250 –258 | 19·5 | 0·9182 | 1·52599 | 1·53784 | 1·52118 | 181·4 | 56 | 24 | 20 | 184 |
| 258 –260 | 19·5 | 0·9260 | 1·53226 | 1·54453 | 1·52750 | 183·9 | 47 | 30 | 23 | 193 |
| 260 –263 | 19·4 | 0·9318 | 1·53637 | 1·54929 | 1·53163 | 189·5 | 40 | 33 | 27 | 197 |
| 263 –268·5 | 19·1 | 0·9324 | 1·53460 | 1·54732 | 1·53004 | 185·3 | 30 | 26 | 44 | 192 |
| 268·5–272 | 11·5 | 0·9478 | 1·54793 | 1·56190 | 1·54270 | 202·6 | 15 | 39 | 46 | 200 |
| 272 –F.B.P. | 10·6 | 0·9725 | 1·56885 | 1·58568 | 1·56345 | 228·6 | — | 65 | 35 | 227 |
| 250 –F.B.P. | 100·0 | — | — | — | — | — | 36 | 33 | 31 | — |

of the peaks by other absorbing substances and the lack of data on pure aromatics of all classes. It is intended to extend the application of this scheme of selective desulphurisation and to improve the accuracy by employing charges of 10 litres or greater.

## ANALYSIS OF UNSATURATED PRODUCTS

With the increasing employment of petroleum as a source of raw materials for the manufacture of synthetic chemicals and the like, it is of considerable advantage to know the hydrocarbon make-up of other than straight run products, *e.g.*, those resulting from processes such as cracking or reforming, etc. The essential difference between such materials is the presence in the cracked or reformed products of an additional class of hydrocarbons, namely, the unsaturateds or olefins. The commonly accepted measure of olefin content involves the estimation of the extent of halogen addition under controlled conditions. Examples of methods include the Wijs and Hanus iodine value and the McIlhiney and the Francis bromine numbers. Methods of estimating aromatics in the presence of unsaturateds invariably include correction factors to be applied, based on bromine number results. One instance of this type is the ASTM method D.875-46T, in which the volume percentage absorption to a mixture of 70 per cent $H_2SO_4$/30 per cent $P_2O_5$ is measured, giving a direct value for the content of aromatics plus unsaturateds. The percentage of unsaturateds is calculated from the bromine number and subtraction gives the percentage of aromatics. This procedure becomes inaccurate when applied to samples of high bromine number and, particularly, in cases where diolefins and styrene homologues are present, but nevertheless, appears to be the most reliable for routine work.

*Gasoline 15° to 225° C*

By applying the D.875 method to a series of fractions throughout the boiling range, it is possible to arrive at a detailed composition in terms of individual groups of hydrocarbons. Bearing in mind the astronomically large numbers of possible isomers within each group, particularly of the

unsaturateds, and the inherent errors in their estimation, the results are considered to be good approximations to the truth. The chief source of error is the spread of boiling point of the unsaturated isomers, the magnitude of which renders any precise divisions into well-defined sections impossible. The direct outcome is that a procedure based on a distillation of the original cracked gasoline cannot yield accurate information regarding the size and shape of the olefin molecules, information of the greatest value in almost all applications of cracked gasoline.

A scheme of analysis has been developed which overcomes these difficulties.[15] The first step is the selective adsorption of the aromatics and olefins on silica gel and the isolation of the naphthenes and paraffins by exhaustive elution with a non-aromatic solvent. The yield of naphthenes and paraffins is analysed by fractionation, etc., in the same manner as for the straight run products. The determination of the aromatic hydrocarbons is accomplished by hydrogenating another portion of the original sample under conditions proved to effect complete saturation of the olefins without action on the other hydrocarbons. The hydrogenated product can be analysed as described for a straight run distillate and naphthene, paraffin, and aromatic contents obtained in detail throughout the boiling range. On hydrogenation, an alkene is converted into a paraffin and a cyclene into a naphthene and, under the conditions employed, the carbon-to-carbon linkages are not disturbed. From the quantities and distribution of the naphthenes and paraffins in the hydrogenated product and similar knowledge with regard to the original sample, the quantities and distribution of the alkenes and cyclenes can be calculated by difference. Typical results obtained by this method are given in Table XI. In the interpretation of these hydrocarbon type compositions, several points must be borne in mind, however :—

(i) The olefinic hydrocarbons are estimated as the corresponding saturated hydrocarbons, the non-cyclic olefins or alkenes as paraffins. Each such paraffin can be derived, obviously, from several olefins, *e.g.*, normal heptane from heptenes, heptadienes, heptatrienes, etc. For simplicity, only the mon-olefins are named in the reported analysis.

(ii) Cyclic olefins or cyclenes are estimated as the corresponding naphthenes. As in the case of the alkenes, each such naphthene represents several unsaturateds, *e.g.*, methyl*cyclo*hexane can represent methyl*cyclo*hexenes, methyl*cyclo*hexadienes, and so on, while higher cyclic olefins may be unsaturated with respect to both ring and side chains. Only compounds of the methyl*cyclo*hexene type are quoted in the reported analysis.

(iii) Aromatic hydrocarbons with unsaturated side chains are estimated as the corresponding aromatic with saturated side chains, *e.g.*, ethenylbenzene (styrene) would hydrogenate to ethylbenzene and be estimated as such. Members of this class are confined to the upper boiling range above 140° C. The contents of the individual xylenes will be unaffected, since no corresponding unsaturated compounds are possible.

The above limitations are of particular significance in the analysis of materials produced under high temperature/low pressure conditions,

TABLE XI

*Hydrocarbon Type Composition of Cracker Gasolines*

| Type | Boiling range, °C | Predominant hydrocarbons | Catalytic cracker gasoline | Delayed coker gasoline | Steam pyrolysed naphtha | Shale spirit |
|---|---|---|---|---|---|---|
| Paraffins | 15– 32·5 | *iso*Pentane | 2·33 | 2·02 | — | — |
| | 32·5– 45 | Normal pentane | 0·42 | 4·77 | — | — |
| | 45– 66 | *iso*Hexanes | 2·77 | 2·51 | 0·33 | 0·87 |
| | 66– 75 | Normal hexane | 0·79 | 3·06 | 0·65 | 5·04 |
| | 75– 85 | Dimethylpentanes | 0·38 | 0·39 | 0·44 | 0·17 |
| | 85– 95 | Methylhexanes | 2·17 | 2·24 | 1·74 | 1·25 |
| | 95–109 | Normal heptane | 0·84 | 3·40 | 2·40 | 6·97 |
| | 109–120 | Methylheptanes | 2·03 | 2·60 | 1·52 | 0·41 |
| | 120–130 | Normal octane | 0·69 | 2·48 | 1·78 | 8·65 |
| | 130–150 | *iso*- and Normal nonanes | 2·32 | 3·99 | 1·80 | 5·14 |
| | 150–175 | *iso*- and Normal decanes | 2·29 | 3·95 | 1·54 | 8·77 |
| | 175–200 | *iso*- and Normal undecanes | 1·84 | 2·40 | — | — |
| | 200–225 | *iso*- and Normal dodecanes | 1·48 | 2·31 | — | — |
| | | Total | 20·35 | 35·12 | 12·20 | 37·27 |
| Naphthenes | 32·5– 66 | *cyclo*Pentane | 0·09 | 0·30 | 0·06 | 0·11 |
| | 66– 75 | Methyl*cyclo*pentane | 0·61 | 0·54 | 0·25 | 0·38 |
| | 75– 85 | *cyclo*Hexane | 0·22 | 0·19 | 0·40 | 0·43 |
| | 85– 95 | Dimethyl*cyclo*pentanes | 0·88 | 0·59 | 1·05 | 0·57 |
| | 95–109 | Dimethyl*cyclo*pentanes and methyl*cyclo*hexane | 0·89 | 1·16 | 1·67 | 1·40 |
| | 109–120 | Trimethyl*cyclo*pentanes and dimethyl*cyclo*hexanes | 0·88 | 0·97 | 0·95 | 0·26 |
| | 120–130 | $C_9H_{16}$ | 0·77 | 1·13 | 0·83 | 1·08 |
| | 130–150 | $C_9H_{18}$ | 1·58 | 2·29 | 1·81 | 1·66 |
| | 150–175 | $C_{10}H_{20}$ | 1·77 | 2·18 | 1·76 | 2·69 |
| | 175–200 | $C_{11}H_{22}$ | 2·54 | 3·34 | — | — |
| | 200–225 | $C_{12}H_{24}$ | 2·19 | 2·31 | — | — |
| | | Total | 12·42 | 15·00 | 8·78 | 8·58 |
| Aromatics | — | Benzene | 0·14 | 0·38 | 13·94 | 1·45 |
| | — | Toluene | 0·91 | 0·76 | 19·94 | 2·36 |
| | — | Ethylbenzene | 0·46 | 0·27 | 4·48 | 0·96 |
| | — | Paraxylene | 0·53 | 0·27 | 2·85 | 0·98 |
| | — | Metaxylene | 1·09 | 0·85 | 7·30 | 0·39 |
| | — | Orthoxylene | 0·48 | 0·62 | 3·52 | 0·91 |
| | 150–175 | $C_9H_{12}$ | 3·92 | 2·53 | 12·21 | 3·99 |
| | 175–200 | $C_{10}H_{14}$ | 4·30 | 2·41 | — | — |
| | 200–225 | $C_{11}H_{16}$ | 5·16 | 2·09 | — | — |
| | | Total | 16·99 | 10·18 | 64·24 | 11·04 |
| Alkenes | 15– 32·5 | *iso*Pentenes | 4·19 | 1·54 | — | — |
| | 32·5– 45 | Normal pentenes | 2·52 | 2·32 | — | — |
| | 45– 66 | *iso*Hexenes | 3·48 | 2·20 | 1·33 | 1·36 |
| | 66– 75 | Normal hexenes | 2·09 | 1·63 | 1·15 | 5·77 |
| | 75– 85 | Dimethylpentenes | 0·10 | 0·11 | 0·09 | 0·05 |
| | 85– 95 | Methylhexenes | 3·77 | 0·63 | 0·54 | 1·56 |
| | 95–109 | Normal heptenes | 2·94 | 2·44 | 0·79 | 4·63 |
| | 109–120 | *iso*-Octenes | 2·51 | 0·00 | 0·32 | 0·91 |
| | 120–130 | Normal octenes | 1·26 | 2·97 | 0·43 | 6·08 |
| | 130–150 | *iso*- and Normal nonenes | 2·81 | 0·18 | 0·32 | 4·78 |
| | 150–175 | *iso*- and Normal decenes | 2·59 | 3·33 | 1·64 | 5·89 |
| | 175–200 | *iso*- and Normal undecenes | 0·70 | 0·46 | — | — |
| | 200–225 | *iso*- and Normal dodecenes | 0·51 | 0·62 | — | — |
| | | Total | 29·47 | 18·43 | 6·61 | 31·03 |
| Cyclenes | 32·5– 66 | *cyclo*Pentene | 0·24 | 0·40 | 0·91 | 0·13 |
| | 66– 75 | Methyl*cyclo*pentenes | 0·91 | 0·76 | 0·69 | 0·72 |
| | 75– 85 | *cyclo*Hexene | 0·22 | 0·23 | 0·19 | 0·33 |
| | 85– 95 | Dimethyl*cyclo*pentenes | 1·52 | 0·98 | 0·44 | 0·85 |
| | 95–109 | $C_9H_{12}$ | 1·55 | 1·44 | 0·57 | 1·24 |
| | 109–120 | $C_9H_{14}$ | 1·87 | 0·59 | 0·23 | 0·61 |
| | 120–130 | $C_9H_{16}$ | 1·36 | 1·71 | 0·70 | 1·83 |
| | 130–150 | $C_9H_{16}$ | 3·08 | 1·69 | 0·48 | 2·54 |
| | 150–175 | $C_{10}H_{18}$ | 3·63 | 4·38 | 3·96 | 3·83 |
| | 175–200 | $C_{11}H_{20}$ | 3·20 | 4·91 | — | — |
| | 200–225 | $C_{12}H_{22}$ | 3·19 | 4·18 | — | — |
| | | Total | 20·77 | 21·27 | 8·17 | 12·08 |

since the contents of both dienes and styrenes are much higher than in the case of gasolines from thermal or catalytic cracking processes.

Despite the shortcomings of the selective hydrogenation and adsorption method, extremely useful data have been obtained by its use, the value of which can be judged by reference to Table XI, giving results for a number of process products. In certain cases it has been possible to supplement the data by estimating the total content of one particular class of diolefins, namely the conjugated dienes, by methods based on the Diels–Alder condensation reaction. Both maleic and chloromaleic anhydrides were used as dienophiles, but doubt has been cast on the results, since it is suspected that hydrocarbons other than conjugated dienes can react with these reagents. Ultra-violet spectroscopy has been used in the analysis of cracked $C_5$ cuts, but its development and application in the higher boiling ranges depends on the provision of an adequate number of synthetic hydrocarbons for calibration and standardisation purposes.

*Gas Oils*

The analysis of gas oil fractions containing unsaturateds presents a more complex problem than any of the previous examples. It is not easy to prove, indeed, that unsaturated hydrocarbons exist in a sample of gas oil. Methods for the estimation of the generally accepted criterion of unsaturation, namely, the extent of the addition of halogen, have been developed and shown to yield theoretical results for pure unsaturateds. One such method is the electrometric titration technique, due to Dubois and Skoog, which is applicable to dark coloured oils. The unsaturated hydrocarbons, however, are not the only compounds present in the gas oil boiling range that react with bromine. Sulphur compounds react additively, the degree of reaction varying from compound to compound. A limited number of synthetic samples were available at Sunbury for examination by the Dubois and Skoog method, the results being listed in Table XII. An indication of bromine addition, therefore, does not prove the presence of unsaturateds. The development of a satisfactory method of type analysis for cracker gas oils and similar products is far from complete, and much remains to be done before our knowledge of the chemical make-up of such materials can be augmented.

## Lubricating Oils and Fuel Oils

The extension of the methods of hydrocarbon type analysis to cover the boiling range above gas oil is extremely difficult. The differences between the main classes of compounds become less pronounced as the boiling point is raised, and the changes of combinations of various classes within the one molecule more likely. In addition, the effect of sulphur content and its relation to actual percentage of sulphur compound is increasingly ambiguous. For these reasons few attempts have been made at Sunbury to determine or develop methods of type analysis of lubricating oils, fuel oils, or bitumens. Efforts have been made to correlate selective adsorption results with solvent extraction yields in lubricating oil refining with little success, since the products from the former did not have the same inter-relation-

ship of physical properties as those made from the same feedstocks by solvent extraction processes.

TABLE XII

*Bromine Addition—Sulphur Compounds*

| Compound | Boiling point, ° C | Bromine number | Number of bromine atoms reacting per molecule |
|---|---|---|---|
| *Thiols :* | | | |
| Ethanethiol | 35·04 | 125·5 | 1·0 |
| 2-Propanethiol | 52·60 | 87·2 | 0·8 |
| 2-Methyl-2-propanethiol | 64·35 | 158·1 | 1·8 |
| 1-Propanethiol | 67·82 | 107·5 | 1·0 |
| 2-Butanethiol | 85·15 | 162·6 | 1·8 |
| 2-Methyl-1-propanethiol | 88·72 | 96·4 | 1·1 |
| Butanethiol | 98·58 | 115·5 | 1·3 |
| Pentanethiol | 126·50 | 88·0 | 1·1 |
| *Sulphides :* | | | |
| 2-Thiapropane | 37·32 | 263·9 | 2·1 |
| 2-Thiabutane | 66·61 | 201·5 | 1·9 |
| 3-Thiapentane | 92·07 | 171·0 | 1·9 |
| 2-Methyl-3-thiapentane | 107·22 | 161·8 | 2·1 |
| 3-Thiahexane | 118·50 | 155·9 | 2·0 |
| 2 : 4-Dimethyl-3-thiapentane | 119·8 | 141·1 | 2·1 |
| 2 : 2-Dimethyl-3-thiapentane | 120·0 | 136·1 | 2·0 |
| 2-Methyl-3-thiahexane | 132·1 | 145·1 | 2·1 |
| 5-Methyl-3-thiahexane | 134·0 | 142·7 | 2·1 |
| 4-Methyl-3-thiahexane | 134·0 | 140·5 | 2·1 |
| 4-Thiaheptane | 142·6 | 144·4 | 2·1 |
| 3-Thiaheptane | 144·0 | 140·1 | 2·1 |
| 5-Thianonane | 185·0 | 113·1 | 2·1 |
| 7-Thiatridecane | 260·0 | 68·7 | 1·7 |
| *Cyclic Sulphides :* | | | |
| Thia*cyclo*pentane | 121·2 | 181·0 | 2·0 |
| 2-Methylthia*cyclo*pentane | 132·4 | 146·0 | 1·9 |
| *trans*-2 : 5-Dimethylthia*cyclo*pentane | 138·0 | 138·2 | 2·0 |
| Thia*cyclo*hexane | 141·6 | 127·5 | 1·6 |
| 2-Methylthia*cyclo*hexane | 148·0 | 158·0 | 2·3 |
| Thiophene | 84·0 | 66·8 | 0·7 |
| 2-Methylthiophene | 113·0 | 166·3 | 2·0 |
| 3-Methylthiophene | 115·0 | 151·8 | 1·9 |
| *Disulphides :* | | | |
| 3 : 4-Dithiahexane | 110·0 | 42·3 | 0·6 |
| 5-Methyl-3 : 4-dithiaheptane | 181·0 | 65·2 | 1·2 |
| 6-Methyl-3 : 4-dithiaheptane | 184·0 | 109·0 | 2·1 |
| 2-Methyl-3 : 4-dithiaheptane | 184·0 | 72·1 | 1·4 |
| 2 : 2 : 5 : 5-Tetramethyl-3 : 4-dithiahexane | 192·0 | 71·1 | 1·6 |
| 4 : 5-Dithiaoctane | 195·0 | 136·0 | 2·6 |

It might be argued, and indeed rightly, that even if proved methods of estimating the detailed compositions of heavy oils and residues were available, then application to specific problems of refining and processing would be of doubtful efficiency at this present juncture. It must be remembered, however, that the scope and application of type analysis has grown rapidly during a comparatively short space of time. The increasing

use of petroleum as a source of raw material for the manufacture of synthetic chemicals will undoubtedly have repercussions in the analytical field, with the analyst employing all the possible tools at his disposal, *e.g.*, superfractionation, selective adsorption, infra-red and ultra-violet spectroscopy, magnetic optical rotation, raman spectroscopy, X-ray and mass spectrometry, and electron diffraction.

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DISCUSSION

THE CHAIRMAN : We are fortunate in having with us to-night another very well known worker in the field of hydrocarbon analysis, Dr van Nes of the Amsterdam laboratories of the Royal Dutch-Shell Group, and he has consented to open the discussion for us.

DR K. VAN NES : The two main points I should like to discuss are both concerned with the analysis of saturated products. Mr Rampton makes use of a diagram giving a correlation between the specific refraction, molecular weight, and ring number. I should like to put forward some formulæ which give the same correlation as that represented in Fig 1.

For saturated hydrocarbons and their mixtures, the hydrogen content is an exact measure of the number of rings, because each ring closure gives rise to the loss of two hydrogen atoms. If, in the overall formula of the saturated hydrocarbon or a mixture of saturateds, $R_N$ is the average number of rings per molecule, and $M$ the molecular weight, the hydrogen content can be derived from :

$$\%H = 14{\cdot}37 - 172{\cdot}6(R_N - 1/M)$$

This formula can be written in another way as :

$$R_N = 1 + (8{\cdot}326 - 0{\cdot}5793H)M/100$$

On the other hand, the molecular refraction, $r_M$, is an additive property, and for the hydrocarbon $C_cH_h$:

$$r_M = cr_C \times hr_H$$

where $r_C$ and $r_H$ represents the atomic refraction of one carbon and one hydrogen atom. Making use of Eisenlohr's atomic increments, $r_C = 2{\cdot}418$ and $r_H = 1{\cdot}100$, it is found that :

$$\%H = 112{\cdot}37r_D^{20} - 22{\cdot}623$$

By substitution :

$$R_N = 1 + (0{\cdot}2143 - 0{\cdot}6510r_D^{20})M$$

This formula shows the relation between the average number of naphthene rings, the specific refraction, and the molecular weight, and gives exactly the same information as Mr Rampton's Fig 1. It is necessary to understand the assumptions used in deriving such a formula. These are, first, that the starting material consists of saturated hydrocarbons, secondly, that molecular refraction is really an additive property, and thirdly, that the atomic refractions of Eisenlohr are reliable. The first two assumptions are sound, and the third was investigated some time ago in Amsterdam. The conclusion arrived at was that Eisenlohr's values are not reliable, which is not surprising when it is realized that Eisenlohr determined his values in 1912, and in the course of forty years such values become entirely obsolete.

Our aim was to find reliable atomic increments, especially for the analysis of hydrocarbon mixtures. It is a fundamental question as to what should be used as basis for deriving atomic increments. Should it be a series of synthesized hydrocarbons, or should it be a series of petroleum fractions? This question is important in the whole field of hydrocarbon analysis. We in Amsterdam are convinced that, for the time being, it is better to start with petroleum fractions, the reason being that the number of hydrocarbons studied up till now is limited and their type so specialized that synthesized hydrocarbons are in general not representative of petroleum hydrocarbons.

In our calculations of the atomic refraction for C and H, the values were derived from the relations between hydrogen content and specific refractions of about forty saturated oil fractions. By the method of least squares the relationship

$$\%H = 110{\cdot}48r_D^{20} - 22{\cdot}078$$

was found and is quite different from the formula based on Eisenlohr's data.*

In the analysis reported by Mr Rampton in Table III, it was concluded that the agreement between specific refraction data and $n$–$d$–$M$ data was only reasonable. If the $R_N$ values in this table are compared, there is a mean deviation between $n$–$d$–$M$ method and Eisenlohr's specific refractions of about 0·1 ring, which is unsatisfactory. But if the new relationship :

$$R_N = 1 + M(0{\cdot}2112 - 0{\cdot}6400r_D)$$

* See "Aspects of the constitution of mineral oils" by K. van Nes and H. A. van Westen, pp. 303–10.

is used, the agreement between the specific refraction and the *n–d–M* method is much better. In fact, the mean deviation is only 0·02, which is only one-fifth of that in the paper, which corresponds to the accuracy of the method.

We consider the *n–d–M* method to be a reliable one for the analysis of this type of fraction. Moreover, we believe that for saturated fractions, the lower molecular weight limit is not around 200, as suggested by Mr Rampton, but about 150 or even lower.

Concerning the separation of paraffins and naphthenes, Mr Rampton concludes that the separation obtained by a chromatographic technique, although not quite satisfactory, is encouraging. I agree with that, but feel that thermal diffusion in the liquid state is a far more promising method. About five years ago we found that thermal diffusion was quite satisfactory for the type separation of hydrocarbon mixtures.

In practice, this thermal diffusion is easily carried out. The oil to be separated is placed in a very narrow slit between two vertical cylinders, which are maintained at different temperatures, the inner wall, for instance, being heated with steam, and the outer wall cooled with tap water.

Although the theory of this process is not fully understood, since a theory of liquids is still lacking, it may be said that the shape and the weight of the molecule are the criteria for separation. From a long series of experiments, it was concluded that separations of petroleum fractions into narrow cuts took place according to the number of rings in the molecule. For example, in the separation of the saturated part of an oil in the thermal diffusion column, the molecules arrange themselves according to the number of rings in such a way that the most cyclic molecules are at the bottom of the column and the non-cyclics at the top. Finally, the paraffins are at the top and the mono-naphthenes, di-naphthenes, etc, in order below.

I think there are two reasons why thermal diffusion is to be preferred to chromatography as a type separation method for saturateds. First, the data suggest that separation by thermal diffusion is far more effective. In general, the paraffins are rather easily separated from the rest, and ring numbers up to five have been found in the gas oil range. The other reason is that the thermal diffusion process hardly requires any attention during the separation—the column is simply filled with the oil, the temperature difference between the two walls is established, and after several hours the fractions may be collected.

The difficulty in applying thermal diffusion is in the construction of the column, but the effort spent in its construction is repaid by the results obtained. However, in my opinion, thermal diffusion is the most promising method for type separation according to ring number, and I should like to hear whether Mr Rampton agrees with this.

I should like now to ask a few questions of minor importance. First, there is a question of nomenclature. The term " dicyclic aromatics," which is used by Mr Rampton for indicating naphthalenes, may lead to misunderstanding, since, strictly speaking, a tetraline derivative is also a dicyclic aromatic, because it is an aromatic and has two rings. I suggest, therefore, that the term " dicyclic aromatics " be avoided and " dinuclear aromatics," or simply " di-aromatics," be used.

My next point concerns the analysis of unsaturateds. I should like

to direct attention to a recently published chromatographic method of analysis for unsaturated mixtures in the gasoline and kerosine range, called fluorescent indicator analysis. In chromatography the components of this mixture arrange themselves in this sequence : saturateds, olefins, aromatics. The essence of the method is the addition of a mixture of dyes to the product prior to percolating through silica gel. During the percolation, the various dyes collect at the border lines between the three types of components, giving rise to visible frontiers. The analysis is performed by simply measuring the length of the bands. This method is promising for the analysis of cracked products, and I should like to ask if Mr Rampton has any experience with this method.

MR RAMPTON : Regarding the suggested new values to replace the old Eisenlohr values which we have been using for the lack of something better, I cannot say precisely how the proposal affects our results as quoted. As Dr van Nes has said, obviously it is going to come more in line with the admirable *n–d–M* method, the first ring analysis method that I have seen published, in which some correction at least was put forward for the sulphur content, previous workers having rather glossed over this point.

I welcome the suggestion for the lower limit to 150 for applicability.

As far as separation of paraffins and naphthenes by thermal diffusion is concerned, I am very much attracted to it myself; as a matter of fact, we have one on the design board at Sunbury. But I could not agree more with Dr van Nes when he stressed the difficulties of manufacture. I do not know what slits he has operated with, but you require spacings of the order of about 0·020 inches, and, as you can imagine, a 12-ft column with two tubes, one inside each other with such slit widths between those surfaces, is a tough engineering problem. But I hope before long to have an apparatus, and to get some real results.

As for nomenclature, there seems to be some doubt about whatever one chooses. I deliberately used " dicyclic aromatics " to distinguish between these and the tetralines. At the moment I cannot offer anything better; possibly di-nuclear aromatics is less ambiguous.

The fluorescent dye indicator method that has been coming forward has been tried at Sunbury, but with very partial success. We are using silica gel made in England, of the right mesh as suggested by the method, but we have not tried the Davidson's grade that is used in the States, and we are observing a rather bad feature. It is essential to have a very fine tube packed with 100 to 200-mesh gel, and the chromatogram is developed in this tube, a mixture of dyes having been added to the sample. The chromatographic zones are observed by ultra-violet light, and a yellow or yellowish-green colour indicates the olefins, a deep blue the aromatics, and a very dark red ring develops between alcohol desorbent and the aromatics. The procedure then is to measure these lengths and determine the volume percentages of the components by pure arithmetic. We tried this at Sunbury on a sample which had been analysed by our normal selective hydrogenation and adsorption method. In that method, when we isolate the naphthene and the paraffin components, we deliberately use an aromatic-free kerosine to dilute the naphthenes and paraffins rather than develop an adsorptogram later, because in the large experiments at Sunbury we got

this effect. If you plot refractive index and bromine number of successive filtrates from such adsorptograms, a clear-cut separation of the various classes is not attained, olefins appearing at the end of the naphthene plus paraffin component and still persisting in the aromatic zone. In the few experiments with the fluorescent dye technique we found exactly the same effect occurring, the tendency being to get too low a figure for naphthene and paraffin and too high a figure for the aromatics. This may be due to the gel. We noticed also that according to the detailed method, the amount of gel used amounts only to about 4 g, which, according to our measurements, would only take up about 0·2 g of aromatics plus olefins. We have tried with larger quantities of gel, and we get a better development. But I must agree with Dr van Nes, it is an attractive method for routine analysis, because the existing methods based on acid absorption plus a correction for bromine number are well known to be in error. I am certainly going to continue the work on this fluorescent dye method, because I think it has promise. I believe that methods have been developed with visual indicators as well.

Dr G. G. Bayle : In gasoline fractions boiling from 95° C upwards, one classifies naphthenes according to their reactivity with respect to dehydrogenation. Assuming isomerization to be negligible, the unreactable part covers both naphthenes with five-membered rings and those with geminal substitution in six-membered rings. Reactable compounds are capable of dehydrogenation to the corresponding aromatics, and therefore are hydro-aromatics.

Now it can be seen from Table II, in which the analysis of some gasolines is tabulated, that in the higher boiling fractions the relative abundance of reactable compounds decreases when compared with the amount of unreactable present.

In this connexion, I should like to ask Mr Rampton, first, whether he has experience on more than the two crudes referred to, and whether the same trend is observed there; secondly, whether the same tendency is true in the higher boiling ranges, like kerosine and gas oil; and thirdly, whether he has experience with mixed aromatic–naphthenic compounds—like, for example, tetralins—in the higher boiling fractions.

Mr Rampton : In the analysis of gasolines up to 225° C, it is our experience that with crudes this ratio of unreactables to reactables increases very markedly as the boiling range goes up to 225° C. The chances of getting the unreactable type, including the general substituted compounds, becomes increasingly greater, purely on the grounds of equal distribution of isomers. That is a mathematical fact. Moreover, it is borne out in practice that the ratio increases. I am afraid that we have not done any work above 225° C. We have thought about it, but with the platinum charcoal catalyst operating under atmospheric pressure, if you process any material boiling much above 225° C you have difficulty in removing that material from the catalyst. We are thinking of trying under vacuum conditions, but I am afraid I have no results to give you to-night.

As to the tetralin derivatives, we have not tried yet.

A. J. GOODFELLOW : My own company has recently embarked on the production of 15° cuts in the gas oil range from 200° to 350° C, and we have found surprising divergence between the boiling ranges obtained in different laboratories. Are the boiling ranges as described, say 220° to 225° C, standard IP boiling ranges at standard pressure, or are they, in fact, cut points in a distillation system, and also, if IP standard methods are used, have any difficulties been experienced in reproducibility ?

MR RAMPTON : All these cuts have been obtained on fractionation type columns with a minimum of twenty theoretical plates at 20 : 1 reflux, so in fact they are cut points throughout, and not based on IP distillation. Obviously, it would be useless to attempt any hydrocarbon type analysis work using the IP standard routine distillation, because you would not get the right initial boiling point; you might be somewhere near the final boiling point, but your other temperatures would be in error. We are distilling under vacuum, of course, with conversion by the normal tables, so the answer is that they are true boiling point cut points.

THE CHAIRMAN : There are two questions I would like to ask. Which type of method does Mr Rampton normally favour for molecular weight determination ?

Mr Rampton referred to the use of urea for the attempted separation of paraffin–naphthene fractions with not entirely satisfactory results. Has he tried also thiourea and similar derivatives, which have perhaps rather different selectivities for hydrocarbons ?

MR RAMPTON : As far as molecular weights are concerned, I favour the ebullioscopic method, and I particularly mentioned in my summary the possibility of using the apparatus developed by the Thornton Research Centre.

As far as urea adduction is concerned, I am afraid I have not actually used thiourea itself. I have used urea, but we were rather disappointed because it appeared to adduct such a lot of other substances besides normal paraffins, and the literature in the past two years has rather led me to think that, given proper conditions, you can get urea and thiourea to adduct with anything.

DR D. GALL : Mr Rampton has remarked on the difficulty of doing unsaturation determinations by bromine addition if sulphur compounds are present. I should like to ask him whether he considers that bromine addition would be adequate if he had no sulphur compounds ? I am thinking of measuring unsaturation on Fischer–Tropsch products, which, of course, ought to be sulphur free. If he has any preference for a specific bromine addition method, I should like to hear it.

MR RAMPTON : The bromine number addition method I prefer quite definitely is that due to Dubois and Skoog, based on a electrometric titration, and we are using it as standard in the laboratory. It is quick and very convenient. With alkenes, alkanes, cyclenes, and naphthenes I think you will have no difficulty at all : it would be specific, except of course if

any dienes were present. If they are conjugated, you are going to get a bromine number that is equivalent to mono-olefins and, if not, it is anybody's guess. On the other hand, if you have aromatics present, the only source of trouble would be polycyclic compounds, but if you have no sulphur and very few aromatics I think you are fairly safe with that procedure.

THE CHAIRMAN : In the case of cyclenes, I seem to remember that in the past we have found abnormal bromine and iodine numbers by different methods on materials such as *cyclo*pentene, where there seemed to be some oxidation of the double bond and consequent rupture. Has Mr Rampton come across any difficulties of that type?

MR RAMPTON : Not with the Dubois and Skoog method, because the whole technique is rather different from any of the previous iodine and bromine number methods, and the compound literally does not get a chance to misbehave itself. The bromine is definitely nascent and is taken up immediately, and the moment the end point is reached you have finished, and the compound does not have a chance to react. Certainly, *cyclo*pentene gives the right answer. *cyclo*Pentadiene, of course, will give you the same figure as *cyclo*pentene, because it is conjugated.

B. T. WHITHAM : Has Mr Rampton any idea of the molecular weight distribution of the fractions he obtained in the naphthene–paraffin separation given in Table III, and regarding the column used, were both sections upward percolation, or was one downward and one upward percolation?

MR RAMPTON : We have no knowledge of any segregation of different molecular weight. It was a wide boiling range cut, 120° C, and there is quite possibly some molecular weight segregation there. In any further work at Sunbury we will be using 20° cuts. I suspect there might be a certain degree of segregation.

The answer to the second question is that the percolation is always upwards, we never use downward percolation except when specified, as in the fluorescent dye indicator method.

We prefer upward percolation in all selective adsorption work.

P. MACDONALD : I should like to ask a question in reference to the technique for the hydrogenation of unsaturated materials where the aromatic material is left unchanged, and reference to Mr Rampton's original paper shows that a pressure of about 15 atm was used. Has Mr Rampton any experience of hydrogenation at atmospheric pressure where it is desired to hydrogenate the aromatics as well as the unsaturated aliphatics?

MR RAMPTON : We have not tried hydrogenation in hydrocarbon type analysis work at atmospheric pressure. We developed the nickel tungsten sulphide catalyst method at 250 lb pressure at 435° F and checked that straight run material could be processed unchanged, and that procedure has been adhered to.

THE CHAIRMAN : I think we would all agree that we have had a most interesting and able presentation of this subject by Mr Rampton. The description of the work as " hydrocarbon type analysis " is perhaps a little too specific, because there is very much more than that involved in the results which Mr Rampton has given. In many cases the result leads us half-way towards complete analysis. However, that is both necessary and desirable. The whole matter is, as several speakers—Mr Rampton himself and Dr van Nes—have emphasized, of very considerable and growing importance.

We would, I think, all like to thank Mr Rampton for presenting his paper, Dr van Nes for a very able opening of the discussion, and also all those who have taken part in the discussion. May I ask you to signify your thanks in the usual way.

(The vote of thanks was heartily accorded.)

MR RAMPTON : I cannot let the occasion go by without expressing in public my thanks to my colleagues at Sunbury who have helped me in this work over the last twelve years—in the routine analytical laboratory, the spectroscopic section, and other sections who, from time to time, have worked on various aspects of the problem.

# THE INSTITUTE OF PETROLEUM

AN Ordinary General Meeting of the Institute of Petroleum was held at 26 Portland Place, London, W.1, on 28 January 1953, Dr E. B. Evans, vice-president, in the Chair.

The General Secretary (D. A. Hough) read the minutes of the previous meeting, which were confirmed and signed.

THE CHAIRMAN said: This evening we are fortunate in that we are to hear something about geophysics from Dr D. T. Germain-Jones. Dr Germain-Jones has had a very wide experience of his subject. He joined the Anglo-Iranian Oil Company as a geophysicist in 1927, and nearly the whole of his career has been devoted to geophysics. At the moment he is in charge of the geophysical research work at the Anglo-Iranian Research Station at Kirklington Hall.

The following paper was then presented by Dr D. T. Germain-Jones:

## GEOPHYSICS—ITS PROBLEMS AND TRENDS

By D. T. GERMAIN-JONES * (Fellow)

### GENERAL CONSIDERATIONS

DURING the past two years the oil industry has probably spent about £250 million on exploration geophysics, and yet to many people within the industry it is a subject which is still shrouded in mystery. Until the early 1930s, when this new technique for finding oilfields was emerging from its teething stage, it had been no easy task to convince others, including some geologists, that it was no mere transitory phase; to-day it has to be acknowledged that exploration geophysics is the main foundation on which rests the future progress of the oil industry and, therefore, of man's industrial progress as a whole.

The rapidly increasing importance of geophysics in oil-finding is underlined by some figures given last year by Dr S. Hammer in his Presidential address to the Society of Exploration Geophysicists.[1] The success ratios of wells drilled in the hope of discovering new oilfields, determined from an analysis of wells drilled in the U.S.A. during 1947–51, are as follows:—

| Basis | Success ratio |
|---|---|
| Non-technical (random drilling) | 1 in 30 |
| Geological | 1 in 10 |
| Geophysical | 1 in 6 |
| Combined geological and geophysical | 1 in 5 |

Strange as it may seem, the analysis shows that there is still a surprisingly large number of wildcat wells drilled on a non-technical basis. The improvement resulting from the application of geophysics is striking, and when geology and geophysics work in close co-operation the result is most

* Anglo-Iranian Oil Co. Ltd.

impressive. In this connexion it is also worth recording that the expenditure on geophysics is probably of the order of one-eighth of the total cost of oil exploration. Despite the fact that the first oil discovery based on geophysical indications was in 1926, more than half the 8000 million tons of oil discovered in the U.S.A. prior to 1948 were first located by geophysical means.[2]

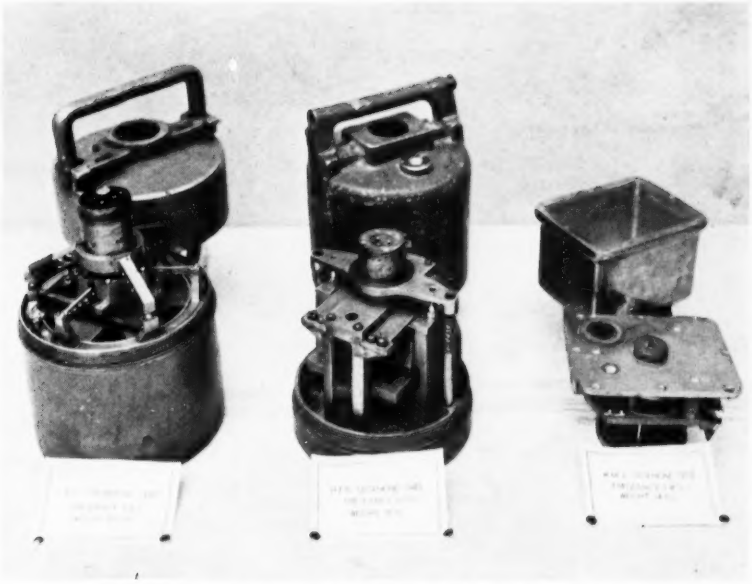
The exploration geophysicist is frequently dubbed a " queer bird " by his oil brethren. This may arise from their fleeting contacts with him : his movements are usually erratic, and it is difficult to understand exactly what he is doing. Most jobs in the industry overlap or dovetail with others, and a man in one of them becomes familiar, to some extent, with the activities of his colleagues; but geophysics seems to be an exception. By the time a newly discovered oilfield is opened up, and the various familiar departmental organizations move in, the geophysicist has moved on to fresh pastures—and " fresh " is the operative word. Not only has the geophysicist, like his geological colleague, the ever-present thrilling hope of finding a new oilfield, but he is always a jump ahead of his other oil brethren, and usually enjoys a life in the open air whose freshness is unpolluted by the smells and smoke which characterize most oilfields.

Within the profession there is marked enthusiasm and co-operation in this task of finding more oil. An example of the efforts made to exchange and discuss information for the benefit of the profession as a whole is the rapid growth throughout the western hemisphere of local sections of the parent Society of Exploration Geophysicists, with its membership of approximately 3000. The same tendency is apparent on this side of the Atlantic, where the recently formed European Association of Exploration Geophysicists, with a founder membership exceeding 300, is rapidly expanding.

## Broad Developments to Date

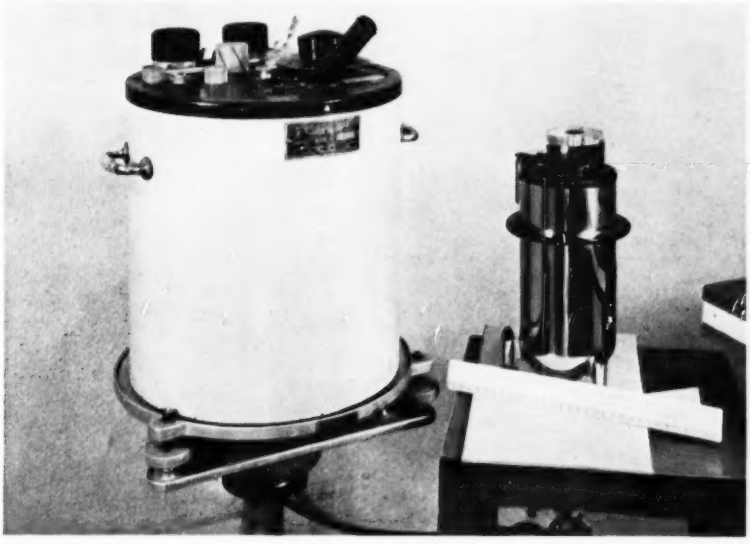
While seismic, gravity, and magnetic methods of prospecting still remain the oil geophysicist's principal tools, each method has undergone considerable developments. The seismic refraction technique first introduced by the Germans a few years after the first world war was largely superseded in America ten years later by the seismic reflection method, and this still remains the most widely employed of all geophysical techniques. Wartime developments of radio position fixing devices and of under-water acoustic equipment have enabled seismic activities to be extended well beyond the limits of the land, thereby making possible the location of the oil reservoirs which lie beneath the continental shelves.

Until about 1935 the torsion balance dominated gravity activity, but by that year the field gravimeter had been developed and quickly superseded the older instrument. Its introduction stepped up the rate of survey by about ten times, and the labour of computation was reduced to a fraction of its former magnitude : and in addition, the range of depth which could be investigated was greatly extended. The gravimeter itself has been improved greatly during recent years, and the development of special temperature compensating devices has led to the production of an instrument which does not require thermostatic control, is the size of



DEVELOPMENTS IN LONG RANGE REFRACTION GEOPHONES BY AIOC

*Left :* E.L.I. geophone, 1939; frequency, 1·2 c/s; weight 80 lb.
*Centre :* H.T.R. geophone, 1945; frequency 3·0 c/s; weight 35 lb.
*Right :* W.M.J. of geophone, 1952; frequency 1·8 c/s; weight 14 lb.



MODERN GRAVIMETERS

*Left :* Frost. *Right :* Worden

[*To face p.* 336.

GEOLOGISTS STUDYING GEOPHYSICAL METHODS AT KIRKLINGTON HALL RESEARCH STATION OF THE ANGLO-IRANIAN OIL CO. LTD.

THE SEISMIC INSTRUMENTAL RESEARCH DEPARTMENT AT KIRKLINGTON HALL

a ½-gal jar and weighs about 6 lb. It is sensitive to about 0·01 milligal, *i.e.*, to a change of one part in 100 million of the total value of gravity. For marine work, land gravimeters have been used in diving bells,[3] but there are also instruments which can be lowered to the sea-bed and levelled and observed by remote control from a boat.[4]

The outstanding development in the magnetic method has been the introduction of the airborne magnetometer.[5] This instrument had reached an advanced stage in its development in America when war broke out, and its potentialities as a submarine detector were quickly recognized and put to use. Before the war was finished it had also been used for its original purpose over petroliferous areas in which the U.S. Navy was interested. Since that time it has been employed over various areas of the world, the total coverage exceeding many times the total area mapped by ground magnetometers for various purposes over the past century.

The sensitivity of the airborne instrument is no less than that of the usual field magnetometer, and it has the great advantage that it can be used over the most difficult terrain, or over water. An area can be surveyed at high speed—about 500 miles of traverse per day—and by making observations over flight patterns at more than one elevation it has been demonstrated that a better estimate of the depths and sizes of the sources of the magnetic anomalies can be obtained.[6]

Attempts to determine directly the presence of oil by the geochemical method which, in effect, seeks " micro-seepages " by analysing the hydrocarbon content of the soil, or soil gases, have not so far met with the success which was anticipated some years ago. It cannot be denied, however, that the fundamental idea is a sound one, and its present recession into a background of research may therefore be only temporary.

The early hopes that electrical methods employing artificial currents might be used for detecting directly the presence of oil—a highly resistive medium—have not been realized, and these methods are at present confined to shallow structural problems and to prospecting for certain metals and minerals. The telluric current method, in which the form and magnitude of the natural earth currents are observed, has been developed extensively by a French concern, and although it has not reached the stage where the presence of an oil saturated rock at considerable depth can be detected, it has provided unusually useful structural information at higher levels. In fact, at least one reliable claim has been made that its use has led to the discovery of oil through such structural information.[7]

An organization in the U.S.A. claims to have perfected a method whereby the periphery of the oil/water boundary of an oilfield can be defined by the reflection and diffraction of radio waves, but, in view of the well-known rapid attenuation of radio waves when passing into the earth, the claim is being treated with extreme caution.[8]

There are reports also of encouraging results having been obtained by an airborne radioactivity method, in which continuous $\gamma$-ray recordings are made along parallel flight lines, or over a grid of lines, the altitude varying between 150 and 500 ft. Experience has shown that a halo of abnormal radioactivity is frequently registered around an oilfield. The idea is novel and fascinating, and has been tried, apparently with success, in Texas and Canada.[9]

## The Present Position and Future Problems

It is frequently stated that our present proved reserves of oil will last only fifteen or twenty years : that consumption is rising rapidly and that, somehow, a lot more oil has to be found. At the same time the stage has been reached where a great number of the oilfields which can be located by geological, or the more simple geophysical, means have been found. The problem which faces the oilfinder to-day is therefore not an easy one, and calls for immense effort. It is clear that the oil industry as a whole is recognizing this fact, for during the past two years there has been an unprecedented rise in geophysical activity. The steep increase which occurred in 1951 [10] suggests that during the past year there were probably about 900 seismic and 150 gravity crews operating throughout the world, about 80 per cent of this effort being expended in the U.S.A. and Canada.

Concurrent with the broad developments to date already described, there have been very considerable advances in the finer details of technique; and exploration problems are being tackled successfully to-day which, a few years ago, would have seemed impossible. The success which is now being achieved can be ascribed to :—

(*a*) advances in instrumentation;
(*b*) improvements in field technique;
(*c*) better methods of interpretation;
(*d*) closer co-operation with the geologist.

In the three main fields of geophysical endeavour—seismic, gravity, and magnetic—the sensitivities of the instruments have reached, or even exceeded, the limits which can be usefully employed in practice; but this does not mean that no further progress in instrumentation is possible, and already some impressive advances have been made.

A knowledge of the type of background noise, *i.e.*, its magnitude and relative frequency content, and of the frequencies and magnitudes of the seismic signals which can be recorded in a given area, will help tremendously in deciding the best type of seismic equipment to put into that area, and also furnish information on how best to adjust it for optimum performance. The normal seismic field equipment is not designed to secure this basic information, and in consequence a seismic field party has sometimes spent much valuable time experimenting with unsuitable apparatus in its endeavour to obtain workable results. At least one prominent geophysical contracting company in the U.S.A. has overcome this problem by developing a mobile laboratory with which the relevant information can be secured in advance of the survey; and a proposal is now being examined at the Kirklington Hall, Nottinghamshire, Research Centre of Anglo-Iranian Oil Co., to form a small mobile section, equipped with the necessary instruments, which can be seconded for a while to a field party anywhere, and at any time, to secure the information which will ensure that the party is working along the most efficient lines. The mobile section would make its principal observations simultaneously with those of the field party, from the same shots, and would not interfere with the routine observations. The information which this section could secure would be of value not

only to the field parties, but it would also help greatly the men who are responsible for the design and development of the survey equipment.

Much attention is being devoted to the production of seismic equipment which can be employed in unusually difficult circumstances. The avenue of research and development on instruments for marine prospecting, for example, is a busy one and, as a result, the world's potential oil reserves have been vastly increased. No ordinary equipment will stand up to the extreme cold of a Canadian winter or the heat and humidity of the jungle and swamp in Papua, where fungus grows rapidly on certain types of electrical components and where the accidental immersion of the equipment in the waters of a creek or river is no uncommon occurrence. Boggy muskeg, rugged terrain, and almost impenetrable jungle also demand the highest degree of portability.

These problems have been eased considerably by wartime developments and by technical research organizations sponsored, for example, by the Ministry of Supply. But some of the requirements of instrumentation are peculiar to geophysics itself, and then the geophysicist has to find his own solution. In the U.S.A. the instrument and component manufacturers cater well for the geophysical profession, but this is not the case on the eastern side of the Atlantic; and the position is aggravated by the difficulty in securing dollars for the importation of suitable American equipment. It is well known how the supply in Britain for drilling equipment has improved during recent years, and perhaps the growth of a similar service for the geophysicist might be anticipated. Two or three British firms, fortunately, have shown some interest and are doing their best to serve the geophysicist despite the pressing demands for their normal products. To them the British geophysicist is much indebted.

The continuous stream of patents which are granted in the U.S.A. for new developments in seismic apparatus and in the circuitry of seismic amplifiers demonstrates the great effort which is being made to improve still further the definition of the seismic signal at the expense of extraneous background noise, chief of which is the ever-present ground unrest. This problem is being attacked, also, in other ways, such as the adoption of a number of geophones on each of the channels, the geophones being arranged in a pattern which will effect a certain degree of cancellation of horizontally directed noise but will sum the effect of the seismic signal arriving from depth in an approximately vertical direction. Similarly, experiments on the use of patterns of explosive charges, either in holes or in the air, instead of concentrating the whole charge in one hole, are furnishing encouraging results which may also lead to greater economy in the use of explosive.[11]

The increasing necessity to divert our attention to the location of fields of the stratigraphic trap type has confronted the geophysicist with some difficult problems in field technique and interpretation. The job of locating the limestone reef [12] and sand lens [13] types of structures, for example, about which a lot is written in the American petroleum press, is one which strains the resolving power of the reflection method to its limit. Cases are cited where closures of the order of 30 ft have been established on the beds draped over a deeply buried reef structure, so leading to the latter's discovery; but the odds against present day equipment and techniques repeating such performances, except under ideal conditions, are considerable.

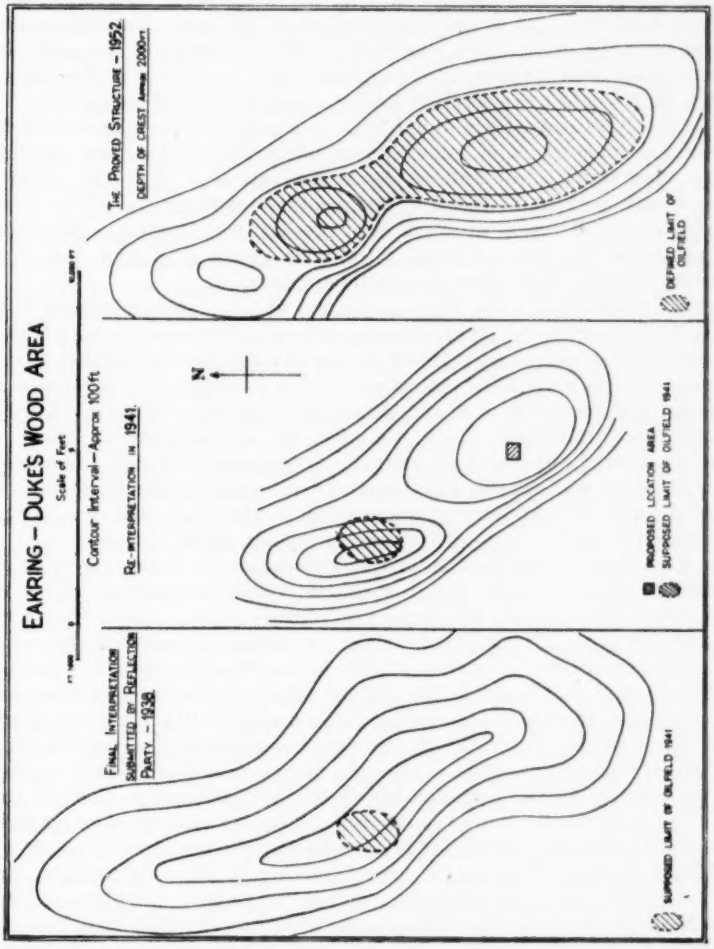
There is no doubt that, provided well-defined and reliable reflections can be recorded, the resolving power of the reflection method exceeds that of the refraction, but there are instances where the latter technique can score heavily over the former. This is a fact which does not seem to be appreciated by quite a number of geophysicists, and experienced reflection operators from America have sometimes expressed surprise that the "obsolete" refraction technique is still practised to a considerable extent by operators east of the Atlantic, and on a scale which, to them, is astonishingly large. In foot-hill country of parts of the Middle East the return of workable reflections with the most modern equipment is practically nil, but big scale refraction technique meets with considerable success, and can outline with sufficient accuracy the huge, deep structures which exist there with a rapidity which far exceeds anything possible with reflection, even if the latter were successful. In a number of the plains areas in the same region, where well-defined reflections appear to have been recorded from great depths, it is becoming increasingly probable that these "deep" reflections are, in fact, multiple reflections from shallower beds. To secure reliable information from greater depths it may eventually become necessary to rely almost entirely on refraction technique.

In Britain, both types of seismic surveying have been undertaken, and parties from two of the foremost seismic reflection contracting companies in the U.S.A. have been employed in addition to AIOC reflection and refraction parties. Despite the small scale of the targets and the great geological complexity of the problem as a whole, the refraction technique has compared favourably with the reflection and, in some cases, demonstrated its superiority.

The needs of the immediate future call for a better understanding of the records which are secured, and for improvements in the technique of interpreting them. Given the opportunity to pursue research on these lines, the geophysicist will not only be in a better position to meet new problems, but could undoubtedly produce a "second crop" of structural targets by applying his new-found knowledge to the masses of records and data which have accumulated from areas surveyed in the past. A typical example of this is the history of the Dukes Wood field, near Eakring, Nottinghamshire. After the Eakring field itself had been found and drilled, an opportunity was afforded to study afresh the seismograms obtained on the original reflection and refraction surveys in the area. It was found that the reflection results could be interpreted in a way which suggested the existence of a further closed anticline just south of the Eakring field, and the meagre refraction evidence available was consistent with this idea. A well was therefore drilled on this new interpretation, and was completed as the biggest producer in Britain up to that time.

The gravimeter has now reached a stage where there is little, or no, advantage in increasing its sensitivity or its portability : and the speed of a gravity survey to-day is governed mainly by the rapidity with which the operator can travel between the observation stations. Obvious ways in which technical advances can be effected are in utilizing closer networks and in improving the interpretation technique to secure greater resolution; and, judging by the number of papers which are being published, it is evident that much work is being done along these lines. A considerable

aid towards improved interpretation would be the development of a gravimeter which could be used in a borehole, and with which the densities of rocks *in situ* at depth could be determined. At the present time it is possible only to use drill cuttings and cores to secure this vital information, and figures so obtained could depart considerable from those which actually


EAKRING – DUKE'S WOOD AREA
Scale of Feet
Contour Interval – Approx 100ft.
Re-interpretation in 1941.
Final Interpretation Submitted by Refraction Party – 1938.
1st. Proved Structure – 1952.
Depth of Crest Area 2000ft.
N
Proposed Location Area
Supposed Limit of Oilfield 1941
Defined Limit of Oilfield
Supposed Limit of Oilfield 1941

A SECOND CROP PROSPECT

prevail under natural conditions. The production of such an instrument is at present engaging the attention of a number of workers, and it will almost certainly make its appearance in due course. A prototype instrument made at Cambridge University has, in fact, already been tested in a borehole [14] and produced, probably, the first gravity borehole observations ever to be made.

The problem of designing an airborne gravimeter, and perhaps one which

will give continuous recordings while being towed by a boat, is difficult because of the extraneous accelerations to which the instrument would be subjected. However, some geophysicists do not think it impossible, and in the course of time the problem might be solved along lines which, at present, cannot be visualized.

While it is generally recognized that the gravity method does not furnish a unique solution to an exploration problem in the sense that the seismic method normally does, there has been a distinct tendency to push the method too far and, at times, to place unwarranted confidence in the results. Though they would not advertise the fact, a number of oil companies who employ geophysical methods would have to admit that they have suffered grievous disappointment at some time or other when subsequent detailed seismic observations, or drilling, have demonstrated that the gravity results meant nothing in terms of sedimentary structure, and have even caused a costly diversion of effort from areas of real interest. However, the gravimeter has proved itself a valuable geophysical tool, but it is important that its limitations should be appreciated.

For oil prospecting over large areas the airborne magnetometer [15] is largely displacing ground magnetometer surveys. The rapidity with which an aerial survey can be carried out makes this method a valuable reconnaissance tool in more than one respect. For example, if a large area is scheduled for prospection where information on the variation of total sedimentary thicknesses would, initially, be of considerable value, a suitably arranged airborne magnetometer survey might furnish the answer in a short time and provide good leads for subsequent seismic work. On the other hand, time and other factors might preclude all ideas of a ground magnetometer survey as a preliminary to seismic investigations.

Much work will continue on methods designed to detect directly the presence of oil, such as the geochemical, electrical, radioactive, and radio wave methods to which reference has already been made. There are undoubtedly types of stratigraphic traps containing commercial quantities of oil which can never be discovered with the resolving power of our present techniques, and it is possible that in the future the research worker will produce an improved direct oil-finding method which will solve the problem.

An important factor which will contribute considerably to future success with present day techniques is that the geophysicist has learned a great deal on how to use his various tools to the best advantage, and on how best to co-ordinate the results of one type of survey with those of another. An example of this co-ordination is furnished by the evidence on which the drilling of Formby Well No. 4, near the coast of West Lancashire, was based. By analysing carefully the evidence of seismic refraction surveys and a reconnaissance gravity survey in the area just east of the well location, a definite statistical correlation was established between the results of the two types of surveys, and an empirical numerical relation was deduced by which gravity changes could be interpreted in terms of depth variations of the deep Carboniferous Limestone. The figures so obtained were applied to the observations secured on a detailed gravity survey near the coast, where seismic refraction work could not be employed owing to the proximity of the sea, and as a result the existence of a very pronounced Carboniferous high was predicted. Well No. 4 proved the existence of this high and, in

addition, demonstrated that the application of the technique just described had resulted in a depth prediction which was remarkably accurate. Needless to say, the solution of a problem like this, where the value of every piece of geophysical evidence has to be assessed most carefully, requires the attention of an interpreter with wide experience and considerable initiative.

Considering the tremendous practical application of geophysical methods, it is surprising how little the geophysicist really knows about some of the fundamental processes by which he secures his data. Particular examples are the complex phenomena associated with a seismic explosion; the initiation and subsequent resolution into wave trains of the seismic disturbance; and the factors which control its propagation and decide its ultimate form and magnitude. These particular problems have been tackled by a number of workers,[11,16] usually with basic assumptions which are much simplified, but a great deal has yet to be done before a really clear understanding is achieved of the processes which obtain in practice. The interpretation of magnetic survey results can frequently be rendered uncertain because large anomalies are sometimes apparently caused by changes in the magnetization of the basement, without any corresponding change in structural configuration so that, here again, fundamental research might improve the interpretative approach. The geophysicist has, in effect, been groping in the dark or, at best, in a half light and, urged on by the insistent demands for results by his employers, he has usually had to approach his problems in an empirical manner which conflicts with the normal instincts of a true scientist. Putting the cart before the horse has certainly produced excellent results so far, but the horse is becoming rather tired, and in the interests of the future it might be well to let him choose his own road for a while and provide the means for him to do so. There is no guarantee that long-term fundamental research will provide all the answers, and it may be difficult at present to visualize what may come out of it. But experience has shown, time and again, that brilliant ideas have been born of such research, and to-day brilliant ideas are required more than ever.

One of the best possible guarantees for the future prosperity of the oil industry is the ever increasing co-operation and understanding between geologist and geophysicist. In the past the geophysicist's problems have been relatively simple compared with those he will have to face in the future, and the good return of geophysical information has enabled him to satisfy his innate need of quantitative data and "facts"; and likewise, also, the geologist's field of relatively simple problems was wide enough to keep him happily occupied. These two oilfinders had therefore comparatively little incentive to co-operate except in a loose fashion. However, the golden era of simple oil structures is passing; data is becoming less quantitative, "facts" are fewer, and nature is gradually nullifying the oil finding surface techniques of the geologist. So the depth probing methods of the geophysicist must be reinforced in the future by the constructive imagination in which the geologist excels; and the new spirit of teamwork already developing is well exemplified by the fact that at the Annual Meeting of the Society of Exploration Geophysicists at Houston last June it was difficult to classify many of the papers as "geology" or "geophysics."

A problem now facing the geophysical profession is the shortage of suitable man-power. On the eastern side of the Atlantic it is understandable, for there is little known about this comparatively new activity; but even in the U.S.A., where a number of universities and institutions offer geophysical training facilities, there is an acute shortage. It has been stated that the cause lies partly in the pessimistic prophecies which have been made in the past concerning a supposed impending shortage of oil, but the general tone of pronouncements in the petroleum press to-day should nullify any discouragement so induced. However, it is also reported that only one in ten or fifteen interpreter trainees in the U.S.A. makes the grade necessary to cope with the geophysical problems,[17] so it is clear that the man-power difficulty will remain for some time to come.

## How the Industry Can Help

The measure of future success achieved in oil exploration will depend greatly on the efforts made by the oil industry's executives in acquiring a deeper understanding of the geophysicist's work and his problems. It should be apparent, from the brief survey already given, that the "hit and miss" principle on which geophysics has been based to a considerable extent in the past can no longer serve adequately, and that the geophysicist in the field must be backed by a strong research and development organization with considerable scope. It has to be realized, for example, that, while the computation and interpretation techniques employed in the past were adequate for the simple structures which were then plentiful, they will no longer suffice for the future: and without an expansion of staff on the interpretation side it will be impossible for the geophysicist to cope with the increased study which the field records and data of the future will require.

It cannot be denied that this lesson is already being learned, as is evident by the establishment of geophysical research and development organizations on an appreciable scale in the U.S.A. and the opening of a centre like Kirklington Hall by the AIOC. The need for such establishments will become increasingly greater, and an oil company which contemplates forming, for the first time, its own geophysical organization, complete with crews, would naturally have to take this point into consideration before discarding the employment of experienced contract parties already backed by such facilities.

The industry can help in other ways. A geophysicist generally has little knowledge of geology, and what knowledge he has is picked up in the course of his work. Similarly, only few geologists have more than a vague idea of geophysical processes and techniques. As already emphasized, this has become a serious matter, and each side is doing its best to remedy the defect. Encouragement from higher levels by facilitating the arrangement of study courses, and affording practical experience in the other man's work, would be well worthwhile. Some time ago, fifteen geologists from three oil companies attended a specially arranged series of geophysical lectures, discussions, and demonstrations at Kirklington Hall, and it was quite evident from their remarks that they had gained for the first time a clear, though perhaps general, picture of geophysical methods

and techniques which would serve them well in their relations with geophysicists, and in their attempts to interpret geophysical maps.

Finally, the oil industry must encourage the scientifically minded youth of to-day to become interested in exploration geophysics as a career, and so ensure a flow of first-class men into this branch of the oil business. Some oil companies already appreciate this necessity, and offer inducement by way of scholarships, grants to geophysical and geological departments of universities, and by part time employment of students on field parties and in research centres during vacations.

## Acknowledgment

This paper is published by kind permission of the chairman of the Anglo-Iranian Oil Co. Ltd. It may be of interest to learn that this company was one of the pioneers in geophysical prospecting. It employed the torsion balance as early as 1923, and by 1927 it had embarked on a considerable programme of exploration using magnetic, electrical, and seismic refraction methods.

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## Discussion

W. J. P. van der Linden : Dr Germain-Jones states that the successes which are now achieved in the finding of oil are due to advances in instrumentation, improvements in field technique, better methods of interpretation, and closer co-operation with the geologists. Thus, success is, in the main, only the result of improvement on, and increased familiarity with, well-known methods. The main difficulties have not been overcome. They are of the same type for all the methods used to-day, and probably will be so for those devised in the future. In order to apply the physical

principle on which the method rests, one has to make broad assumptions as to the conditions of experimentation. And for the handling of the data, one has to assume parameters, sometimes boldly. For instance, in the seismic method one must apply principles of propagation of elastic waves which have been established for media which are elastic, homogeneous, isotropic, and infinite. Certainly, the earth's crust, viewed at the human scale, does not fulfil any of these requirements; the condition of infinity is even paradoxical as we apply the method to determine discontinuities in an assumed infinite medium. At first sight this does not sound very logical. However, it becomes more or less logical when the problem is viewed on a larger scale. In other words, the physical principles are valid within limits which one should never attempt to transgress.

In the handling of the data the parameters can sometimes be measured, as for instance, velocity in a bore-hole, but we must then assume a lateral persistence. That is also a broad assumption, as velocity is coupled with lithology, sedimentation, and structure. Moreover, in practice the geophysicist covers an area before any bore-hole is ever drilled, so velocity must be obtained analytically, statistically, or by rough estimate. If some assumptions are made *a priori*, equations can be written from which the value of the parameters can be obtained. The exact solution is impossible as there are more unknowns than equations.

Better interpretation methods are used in particular cases. A special method of interpretation can sometimes, for a very restricted area, give a structural map which corresponds better with information obtained by other methods. This method is usually devised *a posteriori* and often will not apply to other data, even in the vicinity. So it is good always to keep in mind the old principle : if a structure appears only because of the application of a very special type of correction to the data, or because of special assumptions as to the nature of the seismic paths and the parameters used in the solving equations, beware ! Spend your drilling money elsewhere, if you have any choice.

Some day, someone will find a new principle which will be the basis of a new geophysical method with more resolution power. I feel myself that it is bound to come, and then, when it does, we will all say, " Why haven't we thought of that before ? "

Dr Germain-Jones mentions mobile field laboratories which now operate in the States. These laboratories supply the research and development departments of seismic operators with data enabling them to develop, from scratch, new instruments to operate in areas where no results were obtained before. In the U.S.A. it works very well, because if a crew is in an area and does not obtain results, it can be moved to another one without difficulty and returned to the first area if the laboratories have successfully concluded their research problems. There is no impediment, either for the crew or for the laboratories, resulting from immigration, Customs, import and export permits, and all the difficulties encountered in other areas.

The problem, however, has an intermediate solution. The response of a standard seismic channel is quite broad, and within its limit much could be done to improve the record without having recourse to a brand new type of instrument. Thus, without going to the extent of getting data with

the completely flat system of a field laboratory, it would be a considerable help to supply each of the field crews with a variable-area camera in which records would be obtained with the broadest response afforded by the normal field system. These films, sent to the central research laboratory, would be analysed and the crew advised how to modify its instruments, by changing a few components, to obtain the best results within the scope of those instruments.

A point in the paper which surprised me was that structures of 30 ft closure have been found. It may happen under very special conditions, which I have never met with in my quite long experience, and I cannot help wondering about the number of structures of 30-ft closures over which the seismograph passes without recording them. This brings to my mind the statement of Dr Germain-Jones, in the earlier part of his paper, that the geochemical method did not meet with the success which was anticipated years ago. The connexion is in what is claimed. The principle of the geochemical method was sound; what killed it was that too much was claimed from the method.

Dr Germain-Jones discusses results obtained by the refraction as opposed to those obtained by the reflection method. There were at one time competitive claims between the two methods. We are getting more objective with age, and I think we all agree now that the choice between one or the other method depends primarily on the problem to be solved and on the special conditions in an area. To carry refraction a characteristic refractor is required; in areas where this does not exist, of course, reflection is the only seismic method left. To use reflection one must recognize the reflections through the disturbing surface effects, and in many areas the surface conditions are such that the relatively high frequencies composing the reflected pulse are dissipated in the surface layers, *e.g.*, in Caliche, etc, and only low frequency pulses are transmitted undistorted through the medium. In such areas, if a refractor exists, refraction must be used. So we must be ready to use both methods at any time.

DR GERMAIN-JONES : I cannot recall the exact sources of my information on claims of 30-ft closures, but Dobrin, in his book, implies that closures of this order have been established over reefs. H. M. Thralls has had a good deal to do with the development of a special technique designed to cope with resolution of this order. Though the difficulties are great, it is a degree of resolution which will have to be aimed at if we are to find many small oilfields with our present methods, and I have no doubt that Mr van der Linden had this point in mind when he mentioned the number of small structures which at present the seismograph passes without recording.

I am glad that Mr van der Linden apparently feels that there is still hope for the geochemical method, and that its basis is sound. I certainly think it would be wrong to ignore its possibilities, especially as we are at a stage where structural studies by geophysical methods are sometimes stretching to the limit the resolving power of present techniques.

PROFESSOR V. C. ILLING : I am all in favour of close collaboration between geologists and geophysicists. It was a geologist, namely Dr Barton, who was one of the great early exponents of the use of the torsion balance in

oilfield exploration, and it was due to the insistence of another geologist, namely DeGolyer, that Karcher developed the reflection type of seismic surveys. I think the first instance of the discovery of an oilfield by geophysics was not the Nash Dome in 1926, but the Egbell Field, discovered at least a decade earlier by Professor de Boeckh, who was also primarily a geologist. If there are geologists who decry geophysics, there is also a large body of geophysicists who do not realize the importance of geology. Both are in the wrong. Indeed, the very term " geophysicist " implies a combination of geology and physics, for geology is essential in the interpretation of the physical data because, eventually, these have to be set out in geological terms.

The author has drawn attention to a table, presumably taken from Lahee's published statements, indicating the ratio of success provided by random drilling, geological exploration, geophysical exploration, and a combination of the two latter methods. Such tables may have a limited use, but they must be viewed reservedly. It is very rare indeed that an oilfield is found by only one method, and to reduce the matter to a question of agreed ratios of success is absurd.

I do not agree that random drilling should be completely eliminated. As a geologist, the author naturally prefers geological and geophysical methods, but there are cases where the wildcatter contributes noteworthy discoveries, and the industry would be the poorer if his courage and independence are not allowed to have their outlet.

Some misconceptions are being fostered by too great a concentration on the instrumental side of the work, and too little on the interpretative side. This is perhaps natural, because it is very rare indeed to get that perfect geophysicist, a man in whom geology and physics are equally balanced. If this is not possible, then the next best thing is to have a close collaboration between both geologist and geophysicist, in which the geophysicist takes care of the instrumental side and the geologist of the interpretation.

With reference to the question of accuracy, I doubt very much whether an accuracy of 30 ft can be achieved even in the best of circumstances in reflection seismic surveys. It may be possible within limited areas, but having regard to all the physical conditions and the changes within the rocks which inevitably cause alterations in the velocity gradients, it is obvious that the local facies changes in the formations, which are quite unpredictable until drilling takes place, must inevitably have their effect on the seismic results.

I have such good reason to appreciate what geophysics can do for the geologist that I will not fail to pay tribute to its value, but it is not scientific to over-emphasize a particular truth, nor is it wise to disregard the sources of inaccuracy which are bound to come in when one attempts to treat the geological record as though it were uniform, whereas in fact we know that it is full of the most unpredictable variables.

One of the most prolific causes of trouble in the application of the reflection type of geophysics is the extraordinary uniformity and the beauty of the reflection data in the Mid Continent, and many geophysicists have unwittingly thought that such conditions occur everywhere. It is only when they go to apply the same methods elsewhere that they find that this is rather a unique case and that, in general, the best results can be obtained

where one has a combination of the geophysical tool and the geologist's knowledge of the problems of stratigraphy and structure in the elucidation of the final answer.

The author excluded mention of the Schlumberger surveys from his paper. In this he follows usage in a certain school of thought among exploration geophysicists. None the less, such exclusion is unfair, for in the Schlumberger surveys I feel that physicists have introduced one of the greatest, if not the greatest, aid to the geologist in oilfield technique.

Although I have been somewhat critical of various points in the paper, I feel that the author can be highly commended on the direct and lucid way in which he has delivered his thesis, and I would like to associate myself with his primary purpose, that is, the demand for a closer association between geologists and geophysicists in their work.

DR GERMAIN-JONES : Let me assure Professor Illing that the eminent geologists whom he names are revered by the geophysicist no less than by the geologist for the part they played in establishing the art of geophysical prospecting.

I think Professor Illing is wrong in his statement about the Egbell oilfield. The latter was already a known oilfield when the torsion balance was tested over it—one of many tests conducted over known and unknown structures prior to the 1920s—and I still believe, in common with many others, that 1926 marked the beginning of the era of geophysical oil discoveries, when oil was first produced from the Nash Dome outlined by the torsion balance in 1924. In the latter year seismic refraction also outlined the Orchard Dome.

Professor Illing's opinion about Dr Lahee's success ratio figures is not shared by the majority : the figures have their limitations, but so have many other sets of figures which are drawn up mainly with the object of illustrating the trend of events.

I do not suggest at all that random drilling should be completely eliminated. I agree whole-heartedly that the wildcatter has made a most valuable contribution to our proven oil reserves. I am even willing to accept the probability that he has not yet ceased to find oilfields in areas which both geologists and geophysicists will have discarded as valueless.

I cannot agree with the suggestion that the instrumental side receives too much attention relative to the interpretative. Both receive considerable attention, and it needs to be stressed that without the immense efforts made on the instrumental side it would have been impossible to secure workable records in areas which have now yielded new oilfields. Geophysical interpretation is not only a matter of geological knowledge, but also of mathematics and physics, and had Professor Illing's suggestion been adopted—the geophysicist taking care of instrumentation and the geologist of interpretation—we should certainly not have reached the advanced stage of present-day geophysics.

I can understand Professor Illing having doubts on the matter of 30-ft closures : I find it difficult to believe myself, though I must emphasize that the conditions under which accuracies of this order are claimed are ideal. Under normal conditions, it would not be possible unless one were extremely lucky.

There is a final point raised by Professor Illing on which my ideas do not accord with his nor, perhaps, with those of many other geologists and some geophysicists. In my paper, I dealt with methods of geophysical prospecting, and by that I mean areal surveys carried out on the earth's surface with a view to locating possible oilfields. While geophysics has made immense contributions to the art of Schlumberger logging, this is a technique which follows after the prospecting parties have done their work. Geophysical prospecting is a tool which supplements the work of the exploration geologist; Schlumberger logging supplements the work of the resident geologist and the reservoir engineer. It is a tool which is of more help in the exploitation stage than in the exploration stage of oilfield development, and I cannot be persuaded to place it in the same category as the methods I have discussed in the paper.

W. DOMZALSKI : I think there is one apparent ambiguity in the discussion which consists in identifying the possibilities of geophysics in general, that is, of all geophysical methods, with the sometimes limited possibilities of one, as applied to a particular problem. This is not always clearly appreciated in different industries which could benefit by the use of geophysics. It is not so much a question of controversy between geology and geophysics as the fact that certain standard methods of exploration may not give reliable results unless assisted by additional and less conventional methods. On the whole, I would say that several combined methods such as reconnaissance gravity and/or magnetic survey, followed by seismic and assisted by borehole, geological, and logging information, should give positive results.

The title of Dr Germain-Jones's paper indicates that considerations may be extended beyond the problems of the geophysical exploration for oil, and I hope I shall be justified in giving some prominence to a geophysical trend rapidly gaining in importance, namely, the use of geophysics in shallow exploration, such as civil engineering and mining work. Of course, I realize that actual mining exploration may be of no great interest to oil men, but the application of geophysics in civil engineering is of importance to the petroleum industry.

To quote but one example, large scale engineering construction work such as a refinery will require a detailed site investigation. This site investigation is helped by the geophysical survey. In any problem connected with the determination of depth to the bedrock and investigation of superficial deposits, geophysics is a very valuable tool. From personal experience, I would say that the results obtained justify the use of geophysical methods in shallow exploration work.

DR GERMAIN-JONES : I am glad that Mr Domzalski has emphasized that geophysics has valuable applications to problems outside the oil industry, and I must admit that my paper should have covered these applications.

Geophysics has its application in many other fields—foundation problems, the search for numerous minerals, radioactive and otherwise, the location of faults in the coal-mining industry, the location of water supplies, investigations of the ocean beds, and so on. The application of geophysical methods

to shallow exploration problems has become of great importance, and will result in great saving of time and money.

P. DOCKSEY : I agree with Dr Germain-Jones in his plea for more co-operation between geologists and geophysicists. I think the root of the trouble lies in a point which has not perhaps been sufficiently stressed, and that is the extreme importance of the interpreter in geophysics. Geophysics is too often understood to comprise the operation of carrying out a survey and the extraordinary skill with which the physicist does that. The interpretation, which really is the core of the whole thing, is neither a purely geological nor a purely physical matter, and can only be carried out successfully by somebody who has such a thorough grasp of both that he is a true geophysicist—the man who has got the geo- that Professor Illing wants.

There must be some underlying cause of the fact that the physicist and the geologist do not easily appreciate each other's point of view. The physicist's frequent lack of geological knowledge and geological appreciation has been stressed. May not the other side also be open to an improvement in attitude? The geologist—I speak with diffidence because I know very little about the subject—seems to lean more towards classification than deduction. This affects his outlook and makes it somewhat more difficult for him to sympathize with the physicist's approach.

DR W. L. F. NUTTALL : It is generally recognized that the geologist is essential for the interpretation and co-ordination of geophysical data. Geophysicists find certain reflection or refraction media which require interpretation by making use of geological data observed at the surface or near by. The geologist's main purpose is thus to make deductions.

The author referred to magnetometer surveys and said that, in certain circumstances, it was possible to determine the depth of the basement by flying the aerial magnetometer at different elevations. In my opinion, it is doubtful if such definite results can be obtained. My impression has always been that a magnetometer survey, or an aerial magnetometer survey, may be valuable for defining the size of a sedimentary basement and possibly for determining where certain uplifts of basement occur. I do not know, however, of any case where an oilfield has been discovered by a magnetometer survey or a depth of basement has been determined by this method.

DR GERMAIN-JONES : Airborne magnetometer surveys have an important application to-day in determining the approximate thickness of the sedimentary column in the early stages of a geophysical prospecting programme. Such a survey is being carried out, for example, in Papua, and another is contemplated in East Africa. Estimates of depth can be made from the shape and magnitude of the anomalies registered as a result of changes in the relief of the basement or magnetization contrasts therein. Sometimes an accuracy of about $\pm 10$ per cent is possible, though normally one must expect a much greater order of error. However, for certain purposes this does not matter. For example, an important decision can rest on the question " Is the basement quite shallow, or are there thousands

of feet of sediments ? " and in such a case the airborne magnetometer may give a very quick answer.

Ground magnetometer surveys have sometimes rendered excellent service in the early stages of a large prospecting programme. One case in which a magnetic survey led to the discovery of an oilfield is the Hobbs Field in New Mexico.

MR DOMZALSKI : Perhaps the usefulness of the aerial magnetometer can best be illustrated by reference to the survey in Africa in which I took part. The oil company who had the concession of the area put down a well on purely geological evidence, which, in connexion with the surface configuration, suggested a promising structure. The costs of drilling in primitive conditions and transport over the countryside devoid of roads must have been very high. The well, which was considerably deep, proved dry. Seismic survey followed without positive results. Finally, it was decided to bring in the airborne magnetometer. The whole area was surveyed in a fortnight, previous operations lasting for about two years. It appeared that the well had been put down in the area of igneous intrusions, which were mapped, and the subsequent seismic work was confined to the more promising parts of the country.

There is one more point which I would like to mention. The discussion revolved around the application of geophysical methods for finding structures. In fact, it was said that geophysics is looking for structures. This is a rather narrow conception of geophysics. The results of a survey do not necessarily have to be interpreted in terms of a " structure," the interpretation in terms of stratigraphy and lithology can be attempted. E. E. Rosaire published articles on non-structural petroleum prospecting in *Geophysics*, July 1951 and April 1952.

H. R. CALVERT : As a physicist I would like to ask one small question—a detail about a magnetometer Dr Germain-Jones showed and explained. He had a gravity counterpoise in the magnetometer. How is the effect of the changing gravity eliminated ? It seems to me you find a small change of magnetic effect using the gravity counterpoise and, if the gravity changes slightly, that would affect the results. How do you explain that ?

DR GERMAIN-JONES : The changes in gravity are very much smaller than the changes in magnetic intensity, and, at the same time, the gravity-restoring force is operating at only a very short horizontal distance from the knife edge of the magnet. So, for practical purposes, the gravity counterpoise remains constant.

A. D. SEGALLER : Having given us structural details of the Worden gravimeter, could you give us similar details of the ordinary type of gravimeter, and, in particular, how the minute differences in attraction are measured ?

DR GERMAIN-JONES : All field gravimeters consist, basically, of a spring with a weight suspended on it, though the variations in design of the systems actually employed are many. Some employ the basic principle directly,

and magnify the displacement of the suspended mass, or its rotation as it is displaced, either by optical or electrical means. The Gulf gravimeter, for example, utilizes a helical spring with about twenty or more turns, which is stretched by a weight carrying a vertically disposed mirror. When the weight is slightly displaced there is also a rotation of the system, and this is measured by utilizing a beam of light, which undergoes a series of multiple reflections designed to increase the optical magnification. Other types introduce the principle of astatization in order to reduce the effective restoring force opposing the gravity change, and the Worden meter, which I have described, is one of them. Descriptions of various types of gravimeters can be found in all of the four modern American text-books on geophysical prospecting.

THE CHAIRMAN : I should like to thank Dr Germain-Jones on your behalf for presenting this very interesting paper to us and also express our appreciation to Mr van der Linden, Professor Illing, and all those who have contributed to the discussion.

# STUDIES IN SHALE OIL. PART VII SOME MISCELLANEOUS STUDIES

By Geo. E. Mapstone * (Fellow)

Summary

Since they are formed by the thermal decomposition of more complex materials, the tar bases isolated from Glen Davis cracked shale gasoline might be expected to contain some homologues of pyridine with olefinic side chains. The first part of the work described in this article was therefore carried out in order to determine whether these bases contained any olefinic side chains.

A study of reactions with permanganate in acid and alkaline solution, with iodine, bromine, or chloramine-T, proved the reactivity of the side chains, and the probable presence of approximately 1·5 mol per cent of olefinic bases.

The tar bases isolated from the shale naphtha do not appear to be significantly different from those from the cracked shale gasoline, except that they were free from olefinic homologues.

Methanol can be used as a selective solvent for the extraction of other compounds,[2] and has the advantage of being only slightly soluble in hexane, higher paraffins, and naphthenes.[3] In the third stage of the work, it is shown that extraction of the crude shale oil with methanol gave an extract which contained a high proportion of tar bases and other high-specific-gravity components of the oil. The other constituents of the oil appeared to be almost completely insoluble in methanol.

In the next stage of the work, indoles have been detected in shale oil, and a new test for indoles (or pyrroles) is described, based on the formation of a brownish purple colour with quinone.

The tar bases present in crude shale oil promote the stability of the emulsions formed during the production of the oil,[5, 6] while other materials present in the aqueous phase have further stabilizing action. The emulsibility of crude shale oil may be decreased by removing the tar bases, initially present, by means of an acid wash, and a further decrease may be obtained by the addition of low-boiling tar bases, such as those present in the hydrolysed acid sludge used for the treatment of the emulsions.[7] The solid residue from the treatment of the crude shale oil emulsions was comprised of resins, carbenes, and asphaltenes, together with some oil, and contained no wax.

In the seventh part of the studies, crude shale oil was treated with an equal volume of sulphuric acid of concentrations ranging from 10 to 98 per cent by weight. Such treatment has been used as the basis for hydrocarbon type analysis, but the results obtained suggest that the method cannot be applied to shale oil.

Some properties of the coke and residuum from the thermal cracking of crude shale oil are given in the final section of the paper. A low-grade bitumen can be prepared from the residuum.

## Introduction

The shale tar bases present in crude shale gasoline constitute a fruitful subject for investigation. For example, Stauffer, using the Hanaus method for determining the iodine numbers of tar bases from Colorado shale oil, indicated the presence of saturated side chains.[1] In view, however, of the known reactivity of the $\alpha$ and $\gamma$ side chains of pyridine homologues, Stauffer's results may be due to substitution instead of addition. For this reason, it was decided to determine whether or not the tar bases isolated from Glen Davis cracked shale gasoline contained any olefinic side chains.

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The shale tar bases, examined in previous papers by the author, were isolated from the acid sludge. This sludge was formed from the sulphuric acid treatment of the gasoline which had been produced by the thermal cracking of crude shale oil. Since the tar bases had been largely produced by the thermal cracking of the higher boiling nitrogen compounds present in the oil, it was possible that the bases present in the naphtha, *i.e.*, the lighter fractions of the crude oil recovered from the shale gas by oil scrubbing, may have had somewhat different properties. When a quantity of the shale naphtha was subjected to the acid treatment process, the opportunity was therefore taken to recover some of the bases for examination.

As methanol and ethanol may both be employed for the removal of aromatics and phenols from coal tar fractions,[2] it was felt desirable to ascertain whether these solvents could have commercial application to shale oil. Methanol can be used as a selective solvent for the extraction of other compounds from paraffins, and it is only sparingly soluble in hexane and higher paraffins and naphthenes.[3]

Although indole and its homologues have been isolated from coal tar, no previous attempt appears to have been made to detect them in crude shale oil. From a consideration of the reactions that can take place during the retorting of oil shale, it had been suggested that indole and its homologues should be present in crude shale oil.[4] The results of the work reported here provide qualitative evidence of the presence of indoles in the oil.

The emulsions formed during the commercial production of Glen Davis shale oil [5, 6] are treated on plant scale by acidifying with the dilute sulphuric acid from the hydrolysis of the acid sludge, which is derived from the gasoline treatment.[7] After boiling, the acid layer is rendered alkaline by dilute ammoniacal liquors, whereby the tar bases extracted from the cracked gasoline, as well as those extracted from the crude shale oil during the emulsion treatment, are liberated. Experiments were therefore carried out to determine the effect of the presence of these additional lower boiling tar bases on the emulsibility of the crude shale oil.

Stossel [8] reported the recovery of valuable microcrystalline waxes from tank bottoms in which they had been concentrated by co-precipitation with, or coagulation by, the asphaltenes in the oil. In the treatment of crude shale oil emulsions and sludges with hot dilute acid, a solid product is produced.[5] This residue from the sludge treatment tanks was then examined to determine whether any waxes could be recovered from it.

The effects of the concentration and amount of acid on oil loss, sludge and tar formation, and the nitrogen and sulphur contents of the crude shale oil, have already been described. It was felt that an examination of the effect of the concentration of sulphuric acid on crude shale oil should be of interest.

After thermal cracking of Glen Davis crude shale oil, there was left either a petroleum coke or a heavy residuum. The petroleum coke was originally burnt as fuel for steam raising, but later was sold for the manufacture of carbide in Tasmania. The residuum was used as fuel oil, no other commercial application having been developed. Some properties of the coke and residuum are recorded, together with the results of some attempts to produce a bitumen from the residuum.

## Experimental

### *Unsaturation of Shale Tar Bases*

(1) *Tar Bases Used*

The tar bases used were isolated from the hydrolysed acid sludge, which was produced from the treatment of the cracked shale gasoline.[9] After distillation, 400 ml of the bases were dissolved in 300 ml of concentrated hydrochloric acid and 150 ml water and the insoluble neutral oils removed. The acid solution was refluxed for 4 hr to polymerize the pyrroles present and then diluted with an equal volume of water and filtered to remove the tar formed (equivalent to approximately 2 per cent of the bases) and further traces of neutral oil. The bases were liberated by the addition of a slight excess of 10N-caustic soda solution, separated, filtered, and distilled. Thus purified, they were free from pyrroles.[10] This treatment may have caused some polymerization of vinyl pyridines which may have been present, but the relatively small loss precluded a greater fraction of the bases being lost.

(2) *Oxidation with Permanganate*

Five ml of 0·151N solution of tar bases in 1N-sulphuric acid were added to 5 ml of 2N-caustic soda and the solution titrated with standard permanganate. The purple colour of the permanganate was readily discharged without the formation of a green manganate colour or a brown manganese dioxide precipitate. By continuing the titration until the pink colour lasted for 10 sec, the permanganate consumption ranged from 0·08 to 0·11 mol per mol of bases. When the same experiment was carried out on solutions of α-picoline and quinalidine, the green manganate was formed immediately and, on further standing, manganese dioxide was precipitated.

Addition of excess permanganate and back titration with ferrous ammonium sulphate gave irregular and unsatisfactory results, so the remainder of the work was carried out by direct titration of the acid solution of the bases with permanganate. Permanganate (0·13N) was added, 1·0 ml at a time, to 5 ml of 0·15N solution of tar bases plus 10 ml of 1N-sulphuric acid at room temperature and the time required for decolorization noted. The rate of decolorization of the added permanganate decreased rapidly with the amount added (Table I), while the time required increased ex-

Table I

| $KMnO_4$, ml | 1 | 2 | 3 | 4 | 5 |
|---|---|---|---|---|---|
| Time, sec. . . . | 3 | 8 | 20 | 55 | 540 |

ponentially with the amount of permanganate until, after the addition of 4 ml, a trace of manganese dioxide precipitation was noted. Precipitation was much more evident after 5 ml of permanganate had been reduced. At the same time, the various volumes of 0·15N tar bases were added to 25 ml of 2N-sulphuric acid and titrated with 0·13N-permanganate at room temperature (approximately 30° C) until the colour of the excess permanganate was permanent for varying times. The results are listed as

equivalents of permanganate reduced per mol of bases (Table II). For subsequent work, 10 ml of 0·15N tar bases plus added sulphuric acid were titrated with permanganate until the colour required 30 sec to be discharged.

TABLE II

*Effect of Time on Reduction of Permanganate*

| Tar base soln, ml | Equivalents of permanganate reduced per mol of bases | | | |
|---|---|---|---|---|
| | Duration 7·5 sec | Duration 15 sec | Duration 22·5 sec | Duration 30 sec |
| 1·0 | 0·63 | 0·76 | 0·84 | 0·84 |
| 3·0 | 0·23 | 0·28 | 0·31 | 0·37 |
| 5·0 | 0·24 | — | 0·37 | 0·41 |
| 7·5 | 0·28 | 0·37 | — | 0·43 |
| 10·0 | 0·33 | — | 0·38 | 0·50 |

Standard solutions of the tar bases, α-picoline, quinoline, and quinalidine, were titrated with standard permanganate. Since the temperature of the titration was found to exert a significant effect on the result, the work was carried out at a series of temperatures (Fig 1). Because of the time required

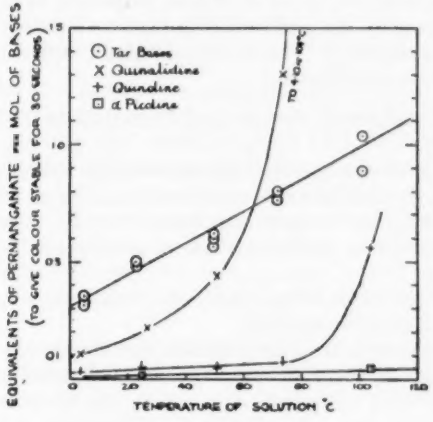


FIG 1

REACTION OF PERMANGANATE WITH BASES

for the permanganate colour to be discharged, the titrations were not taken to completion but to that stage where the colour was stable for 30 sec. The results obtained should, therefore, be indicative of comparative reactivities.

(3) *Action of Iodine*

The addition of 0·1N-iodine in potassium iodide to 0·05N tar bases in 0·1N-hydrochloric acid precipitated a viscous brown oil in the form of small

droplets. On titration with thiosulphate, this oil dissolved very slowly, with the liberation of iodine. The oily product was only slightly soluble in added carbon tetrachloride, but was dispersed, and appeared to be partially dissolved if the latter was added to the tar base solution before the iodine. The end point of the titration was then taken as the point at which the final purple or brown colour was discharged from the carbon tetrachloride. With this procedure, the evolution of iodine from the oily complex was much faster than before, but was still not instantaneous; the tar base–iodine complex decomposed quantitatively during the titration.

The experiment was repeated using 0·05N-α-picoline in 0·1N-hydrochloric acid. This also gave heavy brown oil which slowly liberated the iodine quantitatively to the thiosulphate.

The same results were obtained by adding an iodide–iodate solution to acid solutions of the tar bases and α-picoline, indicating that nascent iodine also did not react irreversibly with the latter.

Alkaline hypoiodite solution reacted with the tar bases, but the results were extremely irregular, suggesting that some oxidation had taken place.

(4) *Bromination*

Decinormal potassium bromide–bromate solution was added to a 0·68N solution of redistilled tar bases in dilute sulphuric acid, and the excess bromine determined by the addition of potassium iodide and back titration with sodium thiosulphate. The results obtained varied considerably, but may be summarized as follows:—

(*a*) the bromine absorbed ranged from 0·05 to 0·57 equivalents per mol of bases;

(*b*) the rate of absorption decreased rapidly with the time of contact but had not reached a constant value after 5 hr at 20° C;

(*c*) increasing the temperature from 2° to 20° C increased the total bromine absorption and the rate of absorption, by approximately 25 per cent;

(*d*) all other factors being equal, approximately constant proportions of the added bromine reacted;

(*e*) with constant bromine addition, the absorption was independent of the amount of bases added over a six-fold range of concentration;

(*f*) the addition of hydrochloric acid to the mixture caused an initial increase in the rate of absorption of bromine, but, after times of contact of 5 min, or more, the extra acid appeared to inhibit the bromination;

(*g*) the presence of ferric chloride did not influence the bromine absorption;

(*h*) in conditions of darkness the bromine absorption was approximately halved;

(*i*) repetition of the work with 0·053N-α-picoline containing 0·034N excess acid gave similar, but less regular, results, the bromine absorbed ranging from 0·06 to 0·60 equivalent per mol;

(*j*) similar results were obtained in light with an 0·061N-pyridine (homologue-free) solution.

(5) *Chlorination*

Since it bleached methyl orange, the chloramine-T had to be removed before the free acid could be titrated. At the same time, the excess chloramine-T had to be determined to correct for the amount of acid used to decompose it. The iodine liberated by potassium iodide formed a slowly dissociating compound with the tar bases as described earlier, so an excess of standard sodium thiosulphate was added with the iodide and the excess titrated with 0·1N-iodine. The method finally adopted was as follows:—

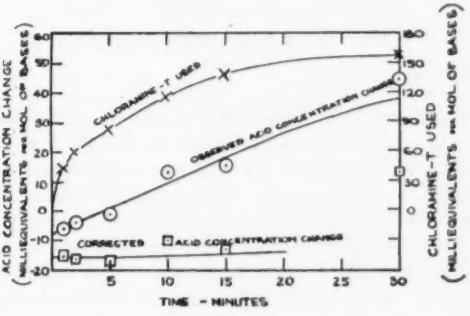


FIG 2

REACTION OF CHLORAMINE-T WITH BASES

Twenty ml of 0·063N tar base solution and 5·0 ml of 0·09N-chloramine-T solution were mixed and allowed to stand for the required time, when the reaction was stopped by the addition of 5·0 ml 0·098N thiosulphate and 0·5 g potassium iodide. The excess thiosulphate was titrated with 0·092N-iodine to a starch end point, the colour destroyed by the addition of one drop of thiosulphate solution, and the free acid titrated with 0·081N-sodium hydroxide to a methyl orange end point.

The blank titrations (zero time) were initially carried out by adding the tar base solution to the chloramine-T after the addition of the iodide and

TABLE III

*Chlorination of Tar Bases with Chloramine-T*

| Reaction time, min | Acid conc change, milli-equivalents per mol bases | | Chloramine-T, milli-equivalents per mol bases |
|---|---|---|---|
| | Observed | Corr | |
| Shale Tar Bases : | | | |
| 1 | − 6 | −15 | 44 |
| 2 | − 4 | −16 | 60 |
| 5 | − 1 | −17 | 82 |
| 10 | +13 | −10 | 116 |
| 15 | +15 | −13 | 138 |
| 30 | +44 | +13 | 157 |
| 240 | +55 | + 6 | 244 |
| α-Picoline : | | | |
| 240 | + 9 | — | 13 |

thiosulphate, followed by the titration with iodine and sodium hydroxide as before. The results thus obtained were somewhat irregular. This was found to be due to the incomplete decomposition of the chloramine-T in the neutral solution before the addition of the tar bases, and was overcome by the addition of 5 ml of 0·1N acid prior to that of the bases, the sodium hydroxide titration being corrected for this additional acid used.

The work was then repeated using a 0·0764N solution of α-picoline, but the reaction was very slow, no significant results being obtained during the first 30 min. All results are presented in Table III and Fig 2.

### *Tar Bases from Shale Naphtha*

(1) *Recovery of Bases*

The acid sludge from the treatment of the naphtha (treatment 4½ lb per brl of 35 I.G., naphtha sp.gr. 0·726 at 60° F, F.B.P. 370° F, basic nitrogen content 0·006 per cent by wt) was hydrolysed on the plant by running into water.[7] At the end of the treatment 4 gal of the dilute hydrolysed acid (free acidity 1·8N) were treated for the recovery of the bases by the procedure described previously,[9] with the addition of some benzene to dissolve the small amount of bases liberated. The benzene was separated from the recovered bases by distillation and the crude bases distilled to separate them from tars recovered with them. The yield was 38 ml, *i.e.*, approximately 60 per cent of theory.

(2) *Examination of Bases*

The properties of the recovered tar bases are given in Table IV. The basic nitrogen content and equivalent weight were determined by dissolving

TABLE IV

*Tar Bases from Shale Naphtha*

| Source | Shale naphtha | Typical from cracked gasoline |
|---|---|---|
| Sp.gr. at 20° C | 0·938 | 0·935 |
| Distillation, ° C: | | |
| 10% over | 172 | 176 |
| 50% over | 186 | 189 |
| 90% over | 211 | 206 |
| Basic nitrogen, % by wt | 10·8 | 8·2 to 10·6 |
| Equivalent wt | 129 | — |
| Pyrroles | Trace | Present |
| Olefinic homologues, mol % | Nil | 1·6 |

a known weight in dilute acid, followed by titration with standard barium hydroxide to thymol phthalein and screened methyl orange.[11] Olefinic homologues could not be detected by the method outlined earlier. The pyrrole content was also lower, but the naphtha bases were identical in odour and appearance, though somewhat more stable in colour than the bases recovered from the cracked shale gasoline.

### *Methanol Extraction*

(1) *High Crude Oil : Methanol Ratios*

The crude shale oil was shaken with the required volume of methanol and allowed to settle at room temperature. The lower oil phase was measured, then separated and washed with hot water to remove the residual methanol. The upper methanol layer was distilled to 152° F, when most of the methanol was removed. Residual methanol was extracted

TABLE V

*Methanol Extraction of Crude Shale Oil*

| Composition | | Methanol phase, ml | Oil phase, ml | Sp.gr. extract at 60° F | Sp.gr. raffinate at 60° F | Ml extract per 100 ml crude |
|---|---|---|---|---|---|---|
| Crude, ml | Methanol, ml | | | | | |
| 100 | — | — | 100 | 1·017 * | 0·902 | Nil |
| 100 | 25 | 26 | 98 | 1·008 | 0·900 | 3 |
| 100 | 50 | 55 | 95 | 1·000 | 0·896 | 5·5 |
| 100 | 75 | 78 | 97 | 0·992 | 0·896 | 8·5 |
| 100 | 100 | 106·5 | 93·5 | 0·982 | 0·893 | 9·5 |
| 75 | 100 | 110 | 62 | 0·980 | 0·895 | 12 |
| 50 | 100 | 109 | 41 | 0·972 | 0·890 | 16 |
| 25 | 100 | 103 | 19 | 0·964 | 0·889 | 20 |

* Extrapolated.

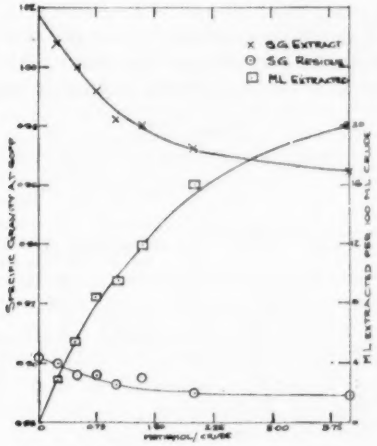


FIG 3

HIGH CRUDE : METHANOL RATIOS

by washing with hot water and the volume of extracted oil measured. This procedure was repeated with oil : methanol ratios ranging from 1 : 4 to 4 : 1. The results are presented in Table V and Fig 3.

Sixteen 100-ml lots of crude oil were then extracted with an equal volume of methanol, using the same method but attaining equilibrium at

100° F. The extract and raffinate oils were freed from methanol by washing with hot water and examined (Table VI). Total sulphur was

TABLE VI

*Properties of Methanol Extracted Crude Shale Oil*

| Oil | Full crude oil | Methanol extract | Raffinate |
|---|---|---|---|
| Proportion, % | 100 | 7 | 93 |
| Sp.gr. at 60° F | 0·899 | 0·987 | 0·893 |
| Total sulphur, % by wt | 0·81 | 1·02 | 0·79 |
| Total nitrogen, % by wt | 0·552 | 1·48 | 0·487 |
| Basic nitrogen, % by wt | 0·112 | 0·36 | 0·094 |
| Distillation, ° F: | | | |
| 20% over | 538 | 500 | 542 |
| 40% over | 630 | 578 | 638 |
| 50% over | 674 | 620 | 680 |
| 60% over | 708 | 662 | 708 |
| Soluble in 80% $H_2SO_4$, % by vol | 44 | 68 | 35 |
| Soluble in 98% $H_2SO_4$, % by vol | 76 | 100? | 76 |

determined by IP 63/42(T), total nitrogen by Kjeldahl,[12] and basic nitrogen by extraction and titration.[11] The solubility of the oils in 80 and 98 per cent sulphuric acid was determined by shaking 5 ml of oil with 5 ml of the acid and centrifuging. With the methanol extract, the insoluble oil was difficult to distinguish in the case of 80 per cent acid. With 98 per cent acid no definite reading could be obtained, possibly because of complete sulphonation. The other two oils were 76 per cent soluble in the 98 per cent acid. The extract oil was not only insoluble in 30 per cent caustic soda, but increased in volume by 12 per cent on treatment with this reagent. The caustic soda solution, however, was found to contain some phenols.

TABLE VII

*Repeated Extraction of Crude Shale Oil*

| Crude, ml | Methanol, ml | Oil extract, ml | Extract sp.gr. at 60° F | Calculated results assuming no loss of oil vol extract, ml | Accumulative vol of methanol as % of crude by vol |
|---|---|---|---|---|---|
| 100 | 100 | 9·5 | 0·982 | 9·5 | 100 |
| 97·5 | 87·5 | 4·0 | 0·974 | 4·1 | 190 |
| 64 | 64 | 2·0 | — | 2·7 | 275 |
| 56 | 56 | 2·0 | — | 3·0 | 360 |
| 53 | 53 | 2·0 | — | 2·8 | 440 |

TABLE VIII

*Results of Cloud Point Tests*

| Ml crude per 100 ml methanol | Cloud point, ° F |
|---|---|
| 0·033 | 75, 78, 77 |
| 0·066 | 86, 88, 85, 87 |
| 0·108 | 115, 101, 103 |
| 0·124 | above 140 |

One hundred ml of crude shale oil were extracted with 100 ml of methanol at room temperature and the quantity of extracted oil determined as before. The raffinate layer was then re-extracted with an equal volume and the procedure repeated until five extractions had been made (Table VII and Fig 4).

Attempts to determine the limiting solubility of crude shale oil in

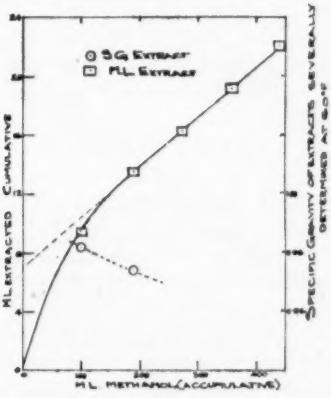


FIG 4

REPEATED EXTRACTIONS

methanol by means of the cloud point test (IP 15/42) gave somewhat variable results (Table VIII), the haziness of the solution appearing to increase on standing at constant temperature. Since this was probably due to crystallization of paraffin wax, the variability of the results can be understood. However, in no case was the crude oil completely soluble in the methanol; residual black specks were left on the sides of the glass even at the boiling point of the solvent.

(2) *Low Crude Oil : Methanol Ratios*

One hundred ml of methanol were placed in a cone-shaped 100-ml centrifuge tube (IP 75/46) which was immersed almost completely in a water bath maintained at 100° F. Crude oil was stirred in slowly from a burette. After 1·0 ml of oil had been added, approximately 0·25 ml of a sticky black residue had settled from the lime-green methanol phase. Curds of this residue only just settled at this concentration, but after 4·65 ml of oil had been added, the residue volume could be read with greater certainty. After 6·9 ml of crude oil had been added, the methanol phase was too opaque to be read except with extra lighting. After 11·55 ml of crude had been added, the readings could be made only in direct sunlight, where the change in the fluorescence of the two layers could be seen. The experiment was repeated at 130° C (Fig 5). Since methanol is known to be only slightly soluble in paraffins and naphthenes [3] and appeared to be dissolved to the extent of less than 1 per cent in the oil, the volume of the oil layer was taken as equal to the insoluble, methanol, portion of the crude shale oil.

A sample of the crude oil was separated into "extract," or "straight chain," and non-extractable oil by means of urea, using the technique

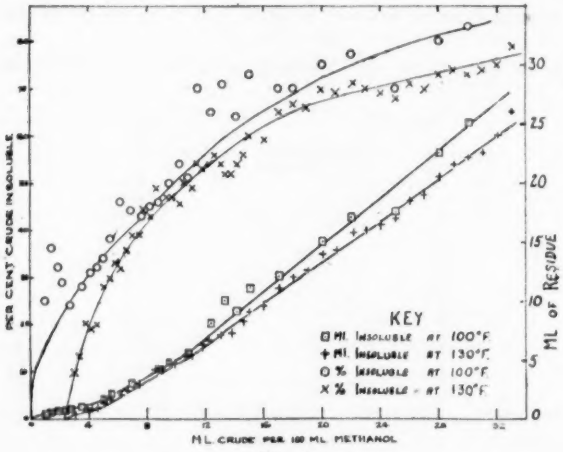


FIG 5

LOW CRUDE : METHANOL RATIOS

described previously.[13] The solubilities of these two fractions in methanol were determined in the same manner as was that of the original oil (Fig 6).

One hundred ml of the dilute acid and caustic-washed gas oil fraction [13] of the crude shale oil were extracted with five successive 100-ml portions of methanol, the volume of the raffinate phase being respectively 100, 90,

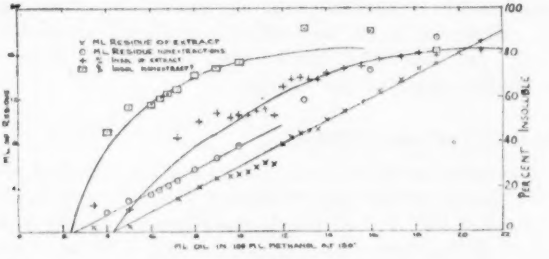


FIG 6

SOLUBILITIES OF UREA FRACTIONATION PRODUCTS

85, 80, and 78 ml after each successive extraction. After removal of the methanol by distillation, 20 ml of extract were recovered. The properties of the fractions are given in Table IX.

The extract was readily and completely sulphonated with concentrated sulphuric acid, but no definite products could be isolated after fusion with caustic potash.

The extract was readily nitrated with concentrated nitric acid and gave a reddish brown solid. However, the results obtained and the properties

TABLE IX

*Extraction of Gas Oil Fraction*

| | Original oil | Extract | Raffinate |
|---|---|---|---|
| Vol, ml | 100 | 20 | 78 |
| Sp.gr. at 60° F | 0·850 | 0·930 | 0·820 |
| Aniline point, ° C | 65 | Below 20 | 76 |
| Bromine No. (UOP) | 5·4 | About 10 | 4·0 |

of the product were similar to those obtained by the nitration of the original oil and to those reported by Gurwitch [14] for the nitration of petroleum fractions.

*Indoles in Shale Oil*

(1) *Initial Tests*

The " indole " content of the 220° to 340° C fraction of crude shale oil was indicated as approximately 0·1 per cent by the quinone test described in the appendix. Neither washing the oil with 2N-hydrochloric acid nor refluxing over solid potassium hydroxide followed by redistillation had any significant effect on the result. However, washing with concentrated hydrochloric acid extracted practically all the " indole," which was recovered along with the tar bases on neutralizing the extract with sodium hydroxide solution. A large amount of a dark red resin (pyrrole polymers) was formed during the extraction with the concentrated acid.

Nine hundred ml of the 220° to 340° C fraction of crude shale oil were extracted with three 150-ml lots of 2N-hydrochloric acid to remove tar bases, were then washed with water and extracted similarly with 2N-caustic soda to remove phenols. The oil was then redistilled and collected in two fractions, to 300° C and 300° C+. The higher boiling fraction contained a much higher proportion of " indoles " as shown by the relative intensity of the colour formed with quinone. Both fractions were extracted four times with half their volume of methanol. In each case the major portion or approximately two-thirds of the " indoles " were extracted with the first wash, but additional washing gave little further extraction.

(2) *Extraction of Indoles (Extract A)*

One litre of the 220° to 340° C fraction of crude shale oil was washed four times with 75 ml of concentrated hydrochloric acid. The fourth extract contained only a trace of " indoles." The extractions were accompanied by the formation of an appreciable quantity of dark red resin.

TABLE X

*Results of Indole Tests*

| Test | Pyrrole, colour | Indole, colour | Extract A, colour | Extract B, colour |
|---|---|---|---|---|
| Quinone | Purple | Purple | Purple | Purple |
| Picrate | Orange | Orange red | Deep red | Deep red |
| Nitroso derivative | Red | Red | Red | Red |
| Ehrlich's test | Red | Red * | Purple | Purple |

* Skatole gives blue colour.[15]

The combined acid extracts were poured into a slight excess of sodium hydroxide solution, undergoing considerable cooling, and the precipitated bases and indoles extracted with ether. The ether extract was washed with water and then extracted with 2N-hydrochloric acid until neutralization of the extract gave a negligible precipitate, and then washed successively with water, sodium carbonate solution, and again with water. Evaporation of the ether gave 5 ml of a dark oil which was completely soluble in methanol. Vacuum distillation of the oil gave a green distillate which became dark red on exposure to air. This distillate responded positively to all tests for indoles (Table X).

(3) *Extraction of Indoles (Extract B)*

One litre of the crude oil fraction 220° to 340° C was saturated with gaseous hydrogen chloride. A red resin was precipitated immediately and, after standing overnight, it was assumed that the polymerization of the pyrroles would be complete. It was then washed with three 100-ml lots of concentrated hydrochloric acid, after which, the oil gave only a very faint test for indoles. The acid washings were neutralized with sodium hydroxide solution and steam-distilled, yielding 5 ml of a green oil which gave a strong positive indication of indole when tested with quinone. The oil was dissolved in ether and extracted with 2N-hydrochloric acid to remove tar bases and then washed with water. Evaporation of the ether left a small amount of oil, which gave positive indications when tested for indole (Table X).

*Shale Tar Bases as Emulsifiers*

(1) *Oil Phase*

To determine the effect of the presence of tar bases, the following crude shale oil samples were prepared :—

A1, crude shale oil, washed with hot water to remove traces of ammonium salts, etc.;

A2, as A1, with the addition of 1 per cent of redistilled light tar bases isolated from the acid sludge from the treatment of cracked shale gasoline; [7]

B1, crude shale oil, washed with 10 per cent sulphuric acid to remove tar bases, then washed with hot water to remove traces of acid;

B2, as B1, with the addition of 1 per cent of redistilled light tar bases isolated from the acid sludge from the treatment of cracked shale gasoline; [7]

B3, as B1, with the addition of 2 per cent of redistilled light tar bases isolated from the acid sludge from the treatment of cracked shale gasoline.[7]

(2) *Aqueous Phase*

To determine the effect of ammonia as present in the retort liquors, the following were used as the aqueous phase :—

*a*, aqueous liquor from the retorts [16] (total ammonia 2·8 lb/1000 gal; free ammonia 0·8 lb/1000 gal);

*b*, distilled water;

*c*, 2N solution of ammonia in distilled water.

(3) *Evaluation*

One hundred ml of the oil and of the water were emulsified together by shaking at room temperature under the same conditions and for the same time for each test. The emulsions were then placed in a water bath at

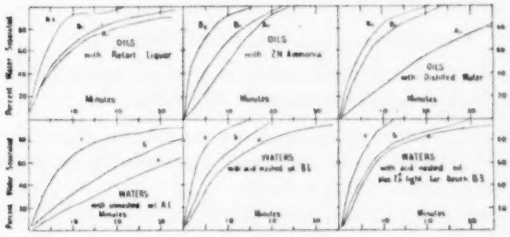

FIG 7

EFFECTS OF DIFFERING COMPOSITION OF OIL AND AQUEOUS PHASES

115° to 120° F and the rate of separation noted. Oil samples A1, B1, and B3 were tested with aqueous liquors *a*, *b*, and *c* (Fig 7) and oil samples A1, A2, B1, and B2 with aqueous liquors *a* and *b* (Tables XI and XII).

TABLE XI

*Effect of Oil Composition on Separation Rate : Results in Order of Increasing Rate of Separation*

| Set | Retort liquor | Dist water |
|---|---|---|
| A | A1 (A2, B2), B1 | — |
| B | A1, A2 (B1, B2) | — |
| C | A1 (A2, B2, B1) | — |
| 1X | A1, A2, B2, B1 | A2, A1 (B1, B2) |
| 2X | A1, A2, B2, B1 | A2, A1, B1, B2 |
| 3X | A1 (A2, B2), B1 | A2 (A1, B1, B2) |

Oil phase :
A1 = Crude oil.
A2 = Crude oil + 1% gasoline bases.
B1 = Acid washed crude oil.
B2 = Acid washed crude oil + 1% gasoline bases.

TABLE XII

*Effect of Composition of Aqueous Phase on Separation Rate : Results in Order of Increasing Rate of Separation*

| Set | Oil mixture | | | |
|---|---|---|---|---|
| | A1 | A2 | B1 | B2 |
| 1 | *a*, *b* | — | — | *a*, *b* |
| 2 | — | — | — | *a*, *b* |
| 1X | *a*, *b* | *a*, *b* | *a*, *b* | — |
| 2X | *a*, *b* | *a*, *b* | — | — |
| 3X | *a*, *b* | — | — | — |
| A | *a*, *b* | *a*, *b* | *b*, *a* | *a*, *b* |

*a* = retort liquor. *b* = distilled water.

All experiments were repeated three times in order to ensure valid results, those presented in Fig 7 being chosen as a typical set with the same factor in common and carried out at the same time. When there was but little difference between two rates of separation, the relative rates were sometimes reversed, but only within the limits of the experimental error of the method.

*Residue from Emulsion Treatment*

The dried solid was analysed, using a method based closely on that of Furby for the evaluation of residuum [17] as follows:—

(1) precipitation of asphaltenes by petroleum ether;

(2) adsorption of resins, oil, and wax soluble in petroleum ether, from action of (1) on fuller's earth;

(3) extraction of the oil and wax from the fuller's earth by boiling petroleum ether;

(4) dewaxing the waxy oil from (3) with acetone–benzene–toluene mixture (40 : 55 : 5) and freezing;

(5) determination of resins adsorbed on fuller's earth by difference after extraction (in this case the resins could not be extracted quantitatively with benzene–ethanol as recommended by Furby);

(6) separation of precipitate from (1) into carbenes and asphaltenes by their solubility in carbon disulphide, the asphaltenes being obtained by difference.

The results are given in Table XIII.

TABLE XIII

*Examination of Residue from Emulsion Treatment*

| | % by wt of dry solid |
|---|---|
| Oil | 23 |
| Wax | Nil |
| Resins | 30 |
| Carbenes | 7 |
| Asphaltenes | 40 |

*Acid Extraction of Crude Shale Oil*

Five ml of the crude shale oil were shaken thoroughly with an equal volume of the acid in a 10-ml graduated centrifuge tube at room temperature (60° to 70° F). The mixture was then centrifuged until there was no change in the volumes of the different layers. In each case, acid, tar, and oil layers separated, and with higher acid concentrations the acid layer separated into two phases, the first sign of this occurring after treatment with 50 per cent sulphuric acid. With the 60 and 70 per cent acid, a white waxy layer soon separated in the oil on centrifuging, but redissolved before the volumes of the different phases became constant.

A portion of the upper oil layer was withdrawn and its specific gravity determined by a pyknometer. No attempt was made to wash out traces of dissolved sulphuric acid or sulphonic acids prior to this determination as, on attempting to do so, emulsions usually formed which were almost impossible to break.

In addition to the work with crude shale oil, a sample of the oil which had been extracted with an equal volume of methanol and the extract was also treated with 80 and 98 per cent acid.

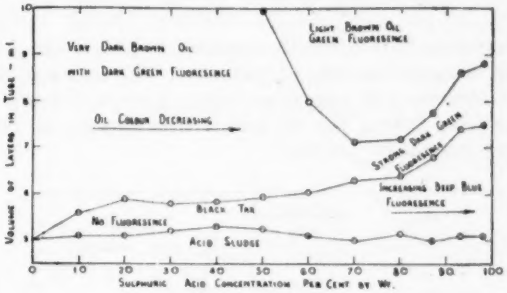
Very Dark Brown Oil with Dark Green Fluorescence
Light Brown Oil Green Fluorescence
Oil Colour Decreasing
Strong Dark Green Fluorescence
Increasing Deep Blue Fluorescence
Black Tar
No Fluorescence
Acid Sludge
Volume of Layers in Tube - ml
Sulphuric Acid Concentration Per Cent by Wt.

FIG 8

EFFECT OF SULPHURIC ACID CONCENTRATION ON OIL VOLUME

The results are presented in Table XIV and Fig 8, and the effect of the time of centrifuging on the volumes of the various phases is shown for

TABLE XIV

*Effect of Sulphuric Acid Concentration on Results of Washing an Equal Volume of Oil*

| Concentration of acid | Time to separate, hr | Acid, ml | Volume of layers | | | Sp.gr. oil at 60° F |
|---|---|---|---|---|---|---|
| | | | Tar, ml | Oil, ml | | |
| 0 | 0 | — | — | 5·0 | | 0·906 |
| 10 | ¼ | 5·1 | 0·5 | 4·4 | | 0·900 |
| 20 | ½ | 5·1 | 0·8 | 4·1 | | 0·892 |
| 30 | 1 | 5·2 | 0·6 | 4·2 | | 0·890 |
| 40 | 1 | 5·3 | 0·55 | 4·15 | | 0·890 |
| 50 | 1 | 5·25 | 0·7 | 4·0 | 0·05 * | 0·892 |
| 60 | 1¼ | 5·1 | 1·95 | 1·95 | 2·0 * | 0·889 |
| 70 | 1½ | 5·0 | 1·3 ‡ | 0·85 | 2·85 * | 0·879 |
| 80 | 1¾ | 5·15 | 1·25 ‡ | 0·8 | 2·8 * | 0·879 |
| 87 | 2¼ | 5·0 | 1·8 ‡ | 0·95 | 2·25 * | 0·882 |
| 93 | 2¾ | 5·1 | 2·3 ‡ | 1·2 | 1·4 * | 0·883 |
| 98 | 3 | 5·1 | 2·4 ‡ | 1·3 | 1·2 * | 0·868 |
| | | | *Methanol-extracted Oil* † | | | |
| 0 | 0 | — | — | 5·0 | | 0·892 |
| 80 | 1¼ | 5·0 | 1·5 ‡ | 0·3 | 3·2 * | 0·870 |
| 98 | 3 | 5·0 | 3·3 ‡ | 0·6 | 1·1 * | 0·853 |
| | | | *Methanol Extracted from Oil* † | | | |
| 0 | — | — | — | — | | 0·987 |
| 80 | 4 | Not separable | | 1·6 ‡ | | 0·987 |
| 98 | 5 | 5·2 | 3·4 | 1·4 ‡ | | 1·211 |

* Upper layer.
† Approximately 7 per cent of oil extracted.
‡ Dark blue fluorescence increasing in intensity with increasing acid concentration.

98 per cent acid in Fig 9. Fig 10 shows the effect of acid concentration on the specific gravity of the oil.

*Coke and Residuum from Thermal Cracking of Shale Oil*

(1) *Coke*

The coke chambers were normally operated to give a coke with a volatile matter content of approximately 8½ per cent. The coke had the characteristic vesicular structure of petroleum coke, a typical sample having an apparent density of 0·94 g per ml and a true density of 1·35 g per ml, indicating a porosity of 30 per cent.

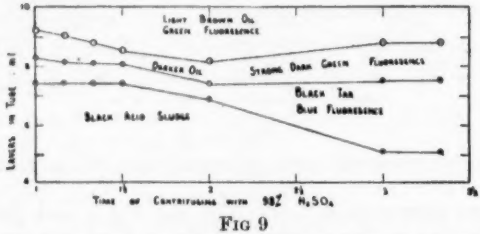


FIG 9

EFFECT OF TIME OF CENTRIFUGING ON OIL SEPARATION

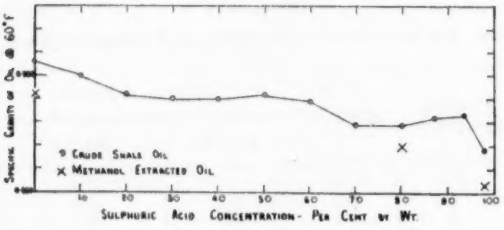


FIG 10

EFFECT OF ACID CONCENTRATION ON SPECIFIC GRAVITY OF OIL

The freshly prepared coke normally contained only a trace of ash, which consisted principally of silica with some iron oxides. No traces of vanadium could be detected.

The coke contained 0·7 to 1·1 per cent sulphur and from 1·0 to 1·5 per

TABLE XV

*Nitrogen and Sulphur in Coke and Residuum*

| | Volatile, % | Nitrogen | Sulphur |
|---|---|---|---|
| Coke . . . . . | 8·25 | 1·50 | — |
| Coke . . . . . | 3·34 | 1·27 | 0·84 |
| Coke . . . . . | 1·0 | 1·03 | — |
| 1·0° API residuum . . . . | — | 1·04 | 1·07 |

cent nitrogen, the latter increasing with the volatile content (see Table XV) and approximately 0·01 per cent phosphorus.

(2) *Residuum*

The cracking plant was initially operated to give a residue of approximately 10° API. Some properties of a typical sample of the residuum, together with the vacuum distillates obtained from it, are given in Table XVI.

TABLE XVI

*Examination of Residuum*

| | Original | Cuts corr to 760 mm | | |
|---|---|---|---|---|
| | | 300° to 400° F | 400° to 550° F | 550° to 700° F |
| Volume, % | 100 | 4 | 14 | 16 |
| Sp.gr. at 60° F | 1·0679 | n.d. | 0·9720 | 1·0160 |
| ° API at 60° F | 1·0 | n.d. | 14·1 | 7·8 |
| Viscosity at 100° F SUS | 10,400 | — | 38 | 154 |

Because of the high viscosity of the residuum samples, routine gravity determinations had to be carried out at temperatures above 140° F, the observed results originally being corrected to 60° F by the petroleum tables. It was noticed that if the gravity was determined at two different temperatures, the calculated values at 60° F did not agree. This anomaly

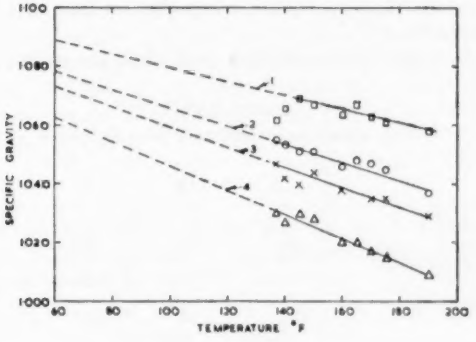


FIG 11

EXPERIMENTAL SPECIFIC GRAVITY–TEMPERATURE RELATIONSHIPS OF RESIDUUM

was investigated by determining the specific gravity of each of several samples at several temperatures and using a normal glass hydrometer. The results were extrapolated graphically to 60° F (Fig 11), and the apparent expansion coefficients calculated (Table XVII). Even after allowing for the cubical coefficient of the expansion of the glass hydrometer, the coefficients show a much greater range, and the heavier samples have much lower coefficients than might be expected from the petroleum tables, or for coal tar. However, these results are in accord with the general experience with the residuum.

TABLE XVII

*Coefficients of Expansion of Residuum*

| Sp.gr. at 60° F | Sp.gr. corr coeff × $10^4$/° F | |
|---|---|---|
| | Observed | Corr * |
| *Residuum :* | | |
| 1·089 | 2·28 | 2·43 |
| 1·078 | 3·10 | 3·25 |
| 1·073 | 3·40 | 3·55 |
| 1·063 | 4·16 | 4·31 |
| *Petroleum :* | | |
| 1·0250–1·0749 | — | 3·4 |
| 1·0750–1·1249 | — | 3·3 |
| *Coal Tar :* | | |
| Crude 1·2 | — | 3·6 |
| Refined 1·2 | — | 3·6 |

* Corrected for cubical expansion of glass 0·14 × $10^{-4}$ ml/ml/° F: correction = sp.gr. × 0·14 × $10^{-4}$/° C.

(3) *Bitumen from Residuum*

Just after the war, there was a shortage of bitumen, so some work was carried out to see if a suitable grade could be produced from the residuum. It was found that it needed little more than topping, as it was very readily overblown, to give a very low penetration, brittle product of high softening point. Even when blowing with a restricted air flow the penetration fell from 160 to 20 in 2 hr.

In order to improve the ductibility and lower the softening point of the

TABLE XVIII

*Some Bitumen Preparations from Residuum*

| | A | B | C | D | E |
|---|---|---|---|---|---|
| Charge, vol per cent : | | | | | |
| Residuum | 95 | 95 | 80 | — | 70 |
| Rerun bottoms and tar * | 5 | — | — | — | — |
| Heavy oil † | — | 5 | 20 | 100 | — |
| Crude oil bottoms ‡ | — | — | — | — | 30 |
| Blowing temp, ° F | 450 | 450 | 475 | 475 | 475 |
| Sp.gr. at 25° C | 1·087 | 1·092 | — | — | — |
| R and B softening point, ° C | 43·5 | 42·5 | 45·1 | 49·4 | 52·2 |
| Penetration : | | | | | |
| 15° C/100 g/5 sec | 33 | 37 | — | — | — |
| 25° C/10 g/5 sec | 86 | 96 | 70 | 68 | 49 |
| Penetration after heating | 19 | 23 | 30 | 43 | 31 |
| Ductility : | | | | | |
| At 1° C cm | 1·5 | 1·75 | — | — | — |
| At 25° C cm | 87 | 105 | 58 | 19 | 90 |
| Solubility in $CS_2$, % by wt | 99·7 | 99·8 | — | — | — |
| Solubility in $CCl_4$, % by wt | 92·0 | 91·8 | 97·7 | 99·7 | 97·7 |
| Flash point open cup, ° C | 155 | 145 | — | — | — |

* Rerun bottoms and tar from hydrolysis of acid sludge blended as produced.

† Heavy recycle oil stream from Dubbs.

‡ Crude shale oil was vacuum distilled at 250 mm mercury with open stream until approximately 14 vol per cent bottoms remained.

product, blends of the residuum with various other heavy oils from the plant were blown. The results of some of these tests are given in Table XVIII.

## Discussion

### *Unsaturation of Shale Tar Bases*

(1) *Oxidation with Permanganate*

With alkaline permanganate, the tar bases were much stronger reducing agents than α-picoline or quinalidine and bound the reduced manganese in a soluble colourless form. This suggested the oxidation of a reactive side chain to a carboxyl group which held the reduced manganese in solution by chelate formation.

The behaviour of the bases towards acid permanganate (Fig 1) confirmed that their reactivity was greater than α-picoline, which was relatively stable, but this could indicate the presence of branched, as well as olefinic, side chains. Quinoline was relatively stable up to about 74° C, after which it was oxidized rapidly, probably in the aromatic nucleus; quinalidine was much less stable than quinoline.

These results demonstrated the reactive character of the side chains of the tar bases, but were insufficient to detect olefinic bonds.

(2) *Action of Iodine*

Although the reaction of iodine with olefinic bonds is usually negligible, because of the enhanced activity of α and γ side chains, it was necessary to check the action of iodine with the tar bases before other methods could be considered. Iodine formed heavy brown oily addition compounds with the tar bases or pyridine which were slowly, but quantitatively, decomposed by thiosulphate. These compounds appear to be analogous to pyridine di-iodide ($C_5H_5NI_2$).[18–20]

(3) *Bromination*

An attempt to detect olefinic side chains by the analytical bromination of the bases was unsuccessful, the bases, α-picoline and pyridine, absorbing approximately equivalent amounts of bromine.

(4) *Chlorination*

As substitution reactions seriously interfered with bromination, the use of chloramine-T in dilute acid solution should have effected substitution of the bases by chlorine, forming hydrochloric acid equivalent to that used, while addition of chlorine to an olefinic bond should have resulted in an equivalent decrease in the total acid concentration. It was found that there was a small initial decrease in the total acid concentration which increased with the time of reaction (Table III, Fig 2), but not as rapidly as the chloramine-T disappeared. This may be explained by the partial hydrolysis of the hydrochloride of the chlorinated bases at the pH of the titration end point, as they would be less basic than the original pyridine homologues.

During the first 15 min of the reaction approximately 1 milli-equivalent

of acid was liberated for each 6 milli-equivalents of chloramine-T reacted. As a first approximation in calculating acid concentration at zero time, this figure gave a final value of approximately 1 milli-equivalent of acid liberated per 5 milli-equivalents of chloramine-T used, corresponding to a 20 per cent hydrolysis of the salt of the chlorinated base. The corrected change in acid concentration then became of the order of $1\frac{1}{2}$ mol per cent of the bases, and was relatively constant over the first 15 min of the reaction (Fig 2).

At the end of 4 hr, the acid concentration change corresponded more closely to a 30 per cent hydrolysis of the salt of the chlorinated product. This trend might have been expected because of the possibility of a higher degree of chlorination, since α-picoline, for example, is attacked very readily by chlorine in aqueous solution to give the penta- and hexachlorpicoline.[21, 22] Dichloracetic acid, carbon dioxide, and nitrogen have been identified among the products of the oxidation of pyridine by chlorine water,[18] indicating another possible explanation for the apparent increase in the extent of the hydrolysis of the chlorinated bases.

Since the accuracy of the titrations was within 3 milli-equivalents of acid per mol of bases, and was probably within 2 milli-equivalents, both the observed and corrected acid concentration changes were significant and confirm the presence of olefinic side chains in the tar bases tested.

It is appreciated that the addition of chlorine to olefinic bonds would not be instantaneous, but any addition reaction would probably be much more rapid than the simultaneously occurring substitution reactions. This was supported by the slight though continued negative acid concentration change during the first 5 min of the reaction (Table III).

The reactivity of the α and γ side chains or the basic character of the pyridine interfered with all the usual chemical methods for the separation of the olefinic homologues. The boiling range of the tar bases indicates the presence of pyridine homologues containing up to six carbon atoms in the side chains, and even if it were possible to isolate the $1\frac{1}{2}$ mol per cent of the olefinic bases, the product would still be a very complex mixture, since it could contain well over 1000 possible pyridine homologues with olefinic side chains, even neglecting geometric and stereo-isomers.

Since this work was completed 2-alkenyl pyridines have been reported in Colorado shale oil.[23] However, the method developed in the present paper gives quantitative results, though it does not differentiate between the various isomers or homologues.

### *Tar Bases from Shale Naphtha*

In general, the properties of the tar bases from the shale naphtha were not significantly different from those from the cracked shale gasoline, and confirmed the previous assumptions that they were pyridine homologues. The additional colour stability of the naphtha bases was probably largely due to their lower pyrrole content,[10] but may have been partly due to the absence of olefinic homologues.

Circumstances prevented a more complete examination of the naphtha bases, but sufficient data are available to indicate that they are essentially the same as those isolated from the cracked shale gasoline.

*Methanol Extraction*

The initial results (Table V, Fig 3) showed that methanol extraction of the crude shale oil effected the removal of constituents of higher specific gravity than the original oil. Examination of the extract (Table VI) indicated a 20 per cent increase in the sulphur content and a large increase in the basic nitrogen content. Assuming an average of 6 per cent nitrogen in the tar bases in the crude shale oil, the extract contained 6 per cent bases by volume. The distillation range of the extract was also significantly lower than that of the original or raffinate oils, and the extract itself was less saturated, as shown by its greater solubility in 80 and 98 per cent sulphuric acid. Although some phenols were extracted by 30 per cent caustic soda solution, the oil absorbed 12 per cent by volume of that reagent. This observation is in agreement with the presence of a large proportion of highly alkylated phenols which are insoluble in caustic.

Repeated extraction with methanol continued to remove a portion of the crude oil (Table VII, Fig 4), suggesting that some constituents were initially partitioned between the oil and methanol and that the methanol was also saturated with the oil. However, the cloud point data (Table VIII) showed that the last fractions of the oil were only slightly soluble in the methanol. This was further borne out by the fractional solubility data at low crude oil : methanol ratios (Fig 5) which also confirmed the effect of temperature on solubility.

To determine whether the paraffin waxes caused the limited solubility of the oil at greater dilution, the straight chain paraffins and olefins were separated by means of urea. The data obtained (Fig 6) showed that the solubility of the wax fraction was approximately twice that of the residual fraction. At the same time, the solubility of the residual fraction at 130° F was the same as that of the original crude oil. This indicated that those constituents of the oil least soluble in methanol were not the paraffin waxes.

Extrapolation of the data of Fig 4 to zero methanol indicated that 7·5 per cent of the oil is infinitely soluble in the methanol. This fraction probably consists of the polar constituents such as the tar bases and tar acids, as indicated from the specific gravity of 1·017 obtained by extrapolation from Fig 3. Allowing for the presence of these components in the methanol extract, estimates of the specific gravity of the remainder of the oil extracted indicate that it is consistently higher than that of the original oil. This supports the suggestion that the methanol extract is more aromatic than the raffinate, which is also indicated by the relative solubilities of the two fractions in concentrated sulphuric acid (Table VI).

*Indoles in Shale Oil*

The results obtained (Table X) showed that pyrrole, indole, and extracts from the crude shale oil all gave the same positive response to the various tests for indole. This was to be expected from the close structural relationship between indole and pyrrole, and the known presence of pyrroles in the shale oil. However, the method for recovering the indole concentrates from the oil by extraction with concentrated hydrochloric acid, especially with extract B where the oil was saturated with hydrogen chloride and

allowed to stand overnight, should have been sufficient to polymerize completely all pyrroles, since indole is polymerized by mineral acids only on heating,[24] while pyrroles are polymerized in the cold. Tetra-alkyl pyrroles are not polymerized, but are sufficiently basic to be extracted by acid along with the pyridine homologues.[25] The chemistry of the reactions also indicates that the tetra-alkyl indoles should not react with the reagents. Although it is still possible that a small amount of pyrroles may have escaped polymerization, the much lower sensitivity of the quinone test to pyrrole than to indole suggests that they would escape detection. The results obtained may therefore be taken as indicating the presence of indoles in shale oil.

Since that fraction of the oil boiling above 300° C contained the greater concentration of indoles (indole b.p. 253° C), it appears that the indoles present are alkylated to an appreciable extent, and probably consist of a complex mixture of nearly all possible isomers, as do the pyridines present in the oil. Attempts to isolate a pure fraction from the indole concentrate were unsuccessful, indicating further the complexity of the mixture obtained. Unfortunately, circumstances prevent further continuation of this work.

### *Shale Tar Bases as Emulsifiers*

The results obtained indicated that acid washing the crude shale oil improved its demulsibility, as was expected from the removal of the tar bases, but the addition of the low-boiling bases, isolated from the gasoline, increased it still further (Fig 7). It therefore appears that, although the crude oil tar bases promote emulsification, the low-boiling bases can have the reverse effect. This is probably due to the selective adsorption of the low-boiling bases at the oil–water interface with the simultaneous displacement of the emulsion-stabilizing high-boiling bases into the body of the oil. These differences are probably further influenced by the small amount of pyrroles in the crude oil, which are polymerized by the acid wash and removed as tar at the same time as the bases.

In practically all cases, the distilled water emulsions broke faster than those containing the ammoniacal liquor, and those containing the 2N-ammonia solution broke faster still. This further increase was quite unexpected, as the use of 2N-caustic soda solutions has frequently given quite stable emulsions in the laboratory. This is probably due to the stabilizing action of phenates, as ammonia is too weak an alkali to extract the high molecular weight tar acids from the oil. At present, no satisfactory explanation can be put forward to explain this action of ammonia.

Emulsions of the retort-liquor in the acid-washed oil broke only slightly faster than those in the unwashed oil. However, when emulsified with distilled water, the rate of demulsification was appreciably faster than with unwashed oil. The presence of the added tar bases caused little further improvement.

In the case of the emulsions of the acid-washed oil containing added light tar bases, there was relatively little difference in the rates of separation of distilled water and of the liquor, but the differences were consistent.

The fastest settling emulsion was that of acid-washed oil containing the added bases and the 2N-ammonia.

*Residue from Emulsion Treatment*

The analysis given in Table XIII shows that the waxes were not concentrated in the solid residue from the treatment of shale oil emulsions and sludges, the main constituents of the residue being resins and asphaltenes. These are probably largely formed by the acid polymerization of unstable constituents of the oil, *e.g.*, pyrroles, during the treatment.

*Acid Extraction of Crude Shale Oil*

Sulphonation of shale oil has been previously observed to give three phases, viz., acid sludge, sulphonic acids, and unreacted oil [13] in the same manner as do petroleum fractions. On washing with even dilute mineral acids a small amount of tar is formed, presumably by the polymerization of pyrroles and other reactive constituents of the oil.[26] This tar apparently dissolved in the sulphonic acid layer when formed, thus continuing this phase over the whole range of acid concentration examined.

The outstanding feature of the results is the separation of the oil layer into two phases on treatment with the stronger sulphuric acid. This separation had not been observed previously, and was seldom detectable until the oil had been centrifuged for some time. The possibility that the lower oil layer was an almost colloidal suspension of some sulphonation product cannot be ruled out, though there was a distinct difference in the fluorescence of the two layers. The results of the treatment of methanol-extracted oil and of the aromatic methanol extract suggest that the lower oil layer may be a solution of alkyl sulphuric, or sulphonic acids in a relatively aromatic portion of the oil, which consequently separated as a separate phase.

The small decrease in the specific gravity of the upper oil layer on increasing the acid concentration may have been due partly to the separation of the oil into two phases or partly to the commencement of attack of the acid on the olefins and/or aromatics. The slightly higher specific gravities of the oils from the 87 and 93 per cent acid could be due to an increased concentration of dissolved sulphonic acids, while the sharp decrease with 98 per cent acid was probably due to the rapidly increasing attack on the aromatics (Fig 10).

Finally, the relatively uniform effect on the volume, or specific gravity, of the oil of changing the acid concentration shows that it is not possible to employ extraction with sulphuric acid as the basis for any accurate analysis of the hydrocarbon type in the oil.

*Coke and Residuum from Thermal Cracking of Shale Oil*

The properties of the coke and residuum given in Tables XV and XVI call for no special comment. However, no explanation can be offered for the differences between the specific gravity temperature coefficients of the residuum and normal petroleum products (Table XVII). These differences are emphasized by the nomograph (Fig 12) correlating the observed and corrected specific gravities with temperature.

Although it was possible to prepare a bitumen from the residuum, the products were invariably of low grade. One interesting property was their low solubility in carbon tetrachloride, indicating the presence of a high

proportion of carbenes (Table XVIII). One possible way of overcoming this might have been to crack less intensively when the residue was to be

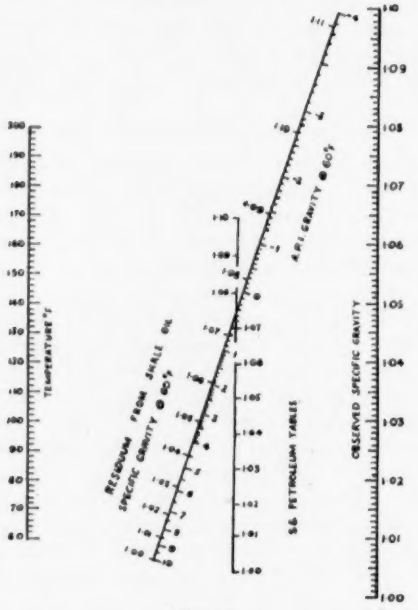


FIG 12

NOMOGRAPH FOR SPECIFIC GRAVITY–TEMPERATURE RELATIONSHIPS OF SHALE OIL RESIDUUM AND PETROLEUM

used for bitumen production, but, as this could not be done without lowering the octane rating of the pressure distillate, the work was not continued.

## ACKNOWLEDGMENTS

The author wishes to acknowledge with thanks the permission granted by the management of National Oil Pty. Ltd. for the publication of the results of the work carried out in their laboratories, and the assistance of various members of the staff in carrying out the experimental work. In particular, thanks are due to: Dr G. Nottes for much helpful discussion on the methanol extraction and for the data reported in Table IX; Mr R. C. Mathews for the specific gravity data of the residuum; Mr D. A. Sutherland for the results of the bitumen experiments; and Mr J. S. Durham for the data reported in Table XIII.

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## APPENDIX

### A New Test for Indole

By Geo. E. Mapstone and W. J. Chodkiewicz

*Detection of Indole with Quinones*

Following the observations of J. D. Bu'Lock and J. Harley-Mason (*J. chem. Soc.*, 1951, 703–12), that quinones formed strongly coloured condensation products with indoles, an attempt was made to derive a test for indoles based on the reaction. *o*- And *p*-benzoquinone, anthraquinone, alizarin, and sodium β-naphthaquinone sulphonate were examined as the quinones. They were tested in methanol solution with 0·1 per cent solution of indole in benzene both at room temperature and the boiling point, and in the presence of added acetic and hydrochloric acids. In each case, the strongest colour was observed with the *p*-benzoquinone so this was used in the remainder of the work. The presence of acid was necessary for development of the colour (which was brownish violet), hydrochloric acid giving better results than acetic acid. The greater the quantity of acid added, the more rapidly the colour developed, but the final colour was weaker. The best results were obtained at room temperature. With coloured samples, it was found advisable to carry out a blank test at the same time. The procedure for the final test was as follows:

Mix 2 ml of 0·5 per cent solution of quinone (*p*-quinone) in methanol with 0·5 ml of the indole solution, and add 5 drops of concentrated hydrochloric acid. The brown to violet coloration develops on standing for 5 min. Carry out the blank test simultaneously, using 2 ml methanol instead of the quinone solution.

The sensitivity of the test for indole in benzol solution is 0·004 per cent by weight. With an alcoholic solution of indole the test is somewhat more sensitive.

*Interference with the Quinone Test*

Various organic nitrogen compounds were examined for interference with the test for indole.

Pyrrole reacted in exactly the same manner as indole, but the test was appreciably

less sensitive. Pyridine, α-picoline, and aniline slowly developed a red colour with a neutral solution of quinone. Addition of concentrated hydrochloric acid to this red solution caused it to become paler or even yellow. Pyrrole-free shale tar bases reacted with the quinone far more rapidly than did the pyridine or picoline, but the colour was still weakened or discharged by the addition of concentrated hydrochloric acid. Redistilled crude shale tar bases developed the colour extremely rapidly on the addition of the quinone. In the presence of acid, however, a colour was still developed, though more slowly, confirming the presence of pyrroles. Diphenylamine gave a slight pinkish tint with neutral quinone solution, but, on the addition of acid, it formed an intense violet colour immediately. This appears to have been due to oxidation to the diphenyl benzidine. In neutral solution ethylenediamine gave immediately a deep red colour with quinone, which was not discharged on acidification. However, in acid solution no colour was formed.

## ERRATUM.

In the *Journal of the Institute of Petroleum* for April 1953, Vol. 39, No. 352, "The Preparation and Properties of Dialkyl Di- and Poly-Sulphides," page 218, second line from bottom:

*for* "m.p. 30–42° C" *read* "30·42° C".

# THE INSTITUTE OF PETROLEUM

## FORTIETH ANNUAL GENERAL MEETING

THE Fortieth Annual General Meeting of the Institute of Petroleum was held at 26 Portland Place, London, W.1, on 21 April 1953. Mr H. S. Gibson, C.B.E., M.A., M.I.Mech.E., presided.

The notice convening the meeting was read by the General Secretary, and the minutes of the Thirty-ninth Annual General Meeting and of the Special General Meetings held on 11 June 1952 and on 10 December 1952 were read, confirmed, and signed by the President.

### ELECTION OF OFFICERS FOR THE SESSION 1953–54

*President*

On the motion of T. Dewhurst, seconded by E. A. Evans, the Council's nomination of Mr H. S. Gibson, C.B.E., M.A., M.I.Mech.E., as president for the session 1953–54 was approved with acclamation.

*Vice-Presidents*

H. S. Gibson proposed and D. L. Samuel seconded that J. A. Oriel, C.B.E., and G. H. Thornley be elected vice-presidents for a term of three years. This was carried unanimously.

*Council*

The President announced that as the result of the ballot the following were declared elected as Members of Council :

A. C. Hartley, C.B.E.
E. LeQ. Herbert
F. Morton
A. J. Ruthven-Murray
G. H. Smith
A. T. Wilford
C. G. Williams
C. S. Windebank

*Honorary Treasurer*

It was proposed by F. L. Garton and seconded by H. E. F. Pracy that Mr G. H. Coxon be re-elected Honorary Treasurer for the ensuing session. This was carried unanimously.

*Honorary Secretary*

It was unanimously agreed, on the proposal of H. Hyams, seconded by G. H. Thornley, that Mr C. Chilvers be re-elected Honorary Secretary for the next session.

*Ex-officio Members of Council*

The President announced that the following had been nominated as ex-officio members of Council to represent the Branches :

| | |
|---|---|
| H. H. Ballard | *Northern Branch* |
| S. A. Berridge | *Fawley Branch* |
| A. W. Deller | *London Branch* |
| N. W. Grey | *South-eastern Branch* |
| E. J. Horley | *South Wales Branch* |
| W. M. Stirling | *Scottish Branch* |

H. S. Gibson proposed that these nominations be accepted and, after seconding by H. Hyams, this was approved without dissent.

## Members Elected or Transferred

The lists of Honorary Members, Honorary Fellows, Members, Fellows, Associate Members, Associate Fellows, and Student Members elected or transferred during 1952 was presented and tabled.

## Report of Council and Accounts

The chairman, proposing the adoption of the Annual Report for the year ended 31 December 1952, said that the report contained interesting and important matters in connexion with the activities of the Institute and he proposed that it be adopted.

F. L. Garton seconded the motion, which was carried unanimously.

G. H. Coxon, the Honorary Treasurer, in presenting the accounts said that the main point on both Balance Sheet and Revenue Account was a general increase in expenditure and particularly in regard to publications.

The Balance Sheet showed that assets had increased to £29,000, an addition of £5000 over the previous year. This was very commendable when high printing and paper costs were borne in mind. With prices now on the downward trend, Mr Coxon thought they could look forward to a reasonably satisfactory year.

The finance of the Institute was closely allied to the publications, and he wished to record a vote of thanks to the chairman of the Publications Committee for his close watch upon costs. He also thanked the chairman of the Finance Committee, who had also kept a watch upon the costs.

There being no questions, D. L. Samuel proposed and F. A. J. Cole seconded, that the accounts be adopted. The motion was carried unanimously.

## Appointment of Auditors

G. H. Coxon proposed, H. Hyams seconded, and it was carried that Messrs Smith and Williamson be appointed auditors at a remuneration to be fixed by the Council.

This concluded the Annual General Meeting.

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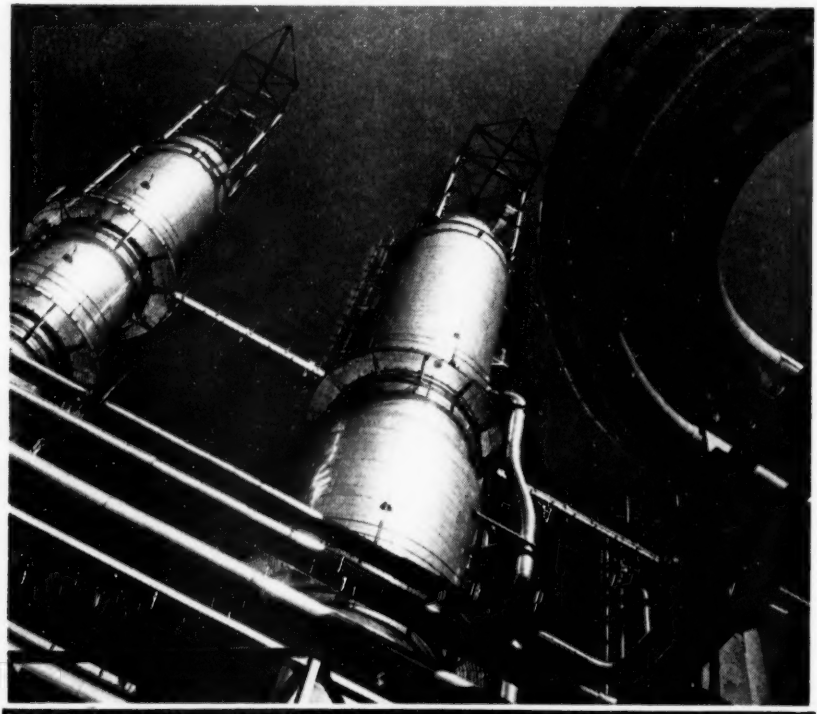

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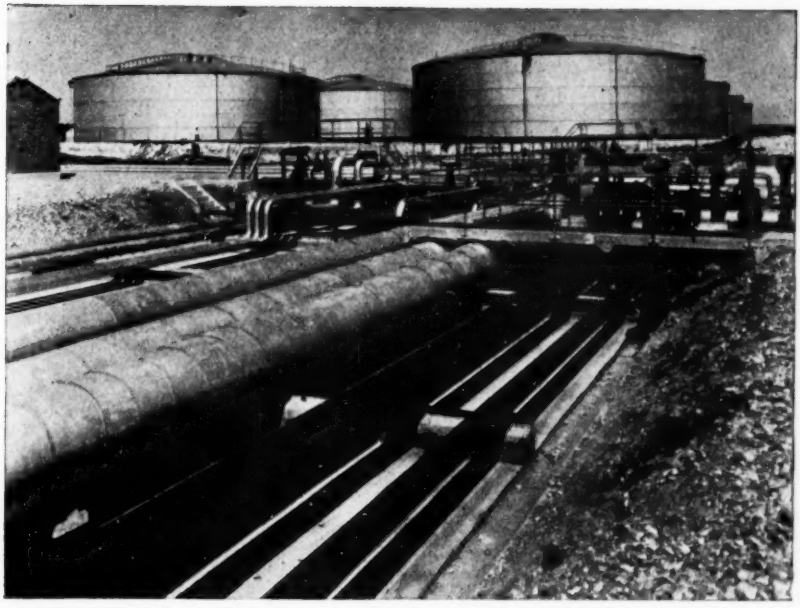

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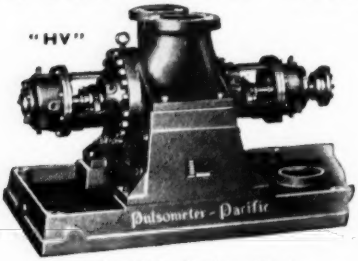


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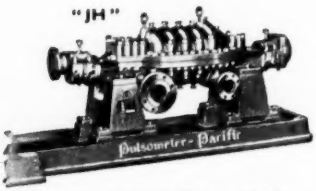


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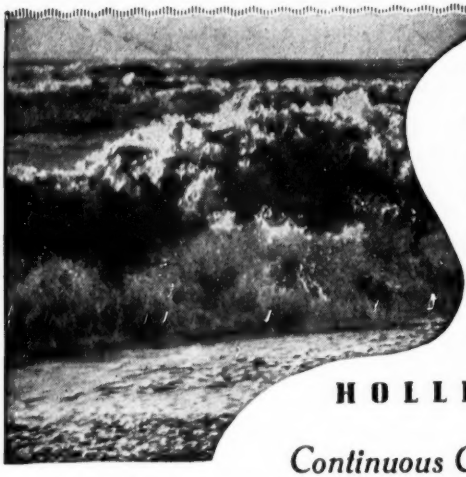

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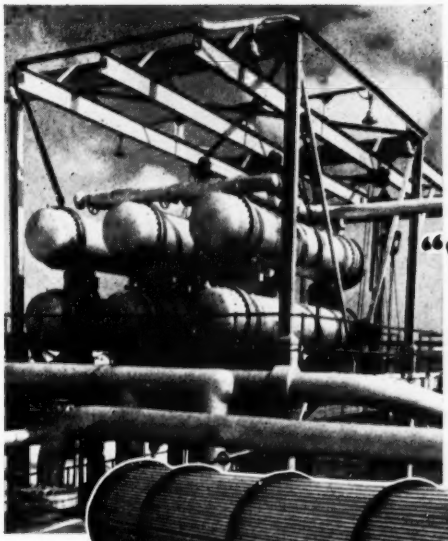

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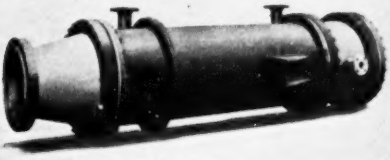

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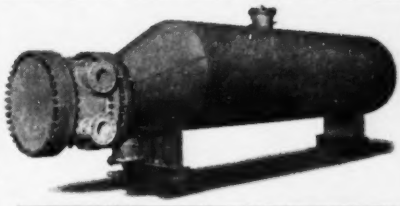

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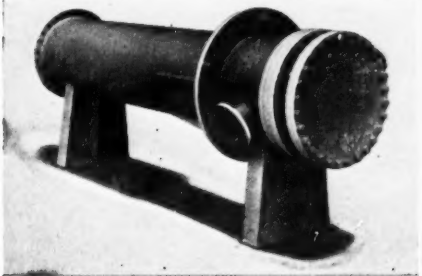

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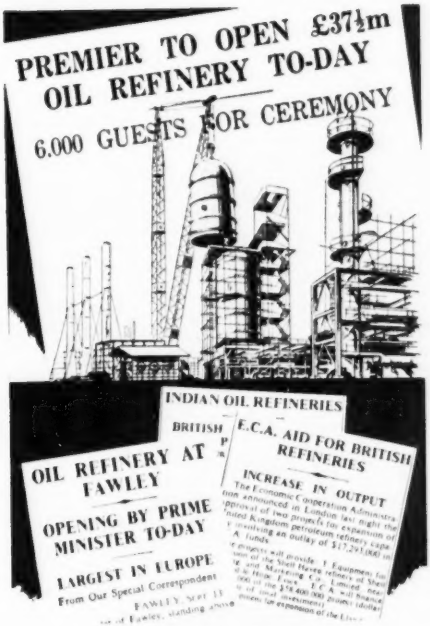


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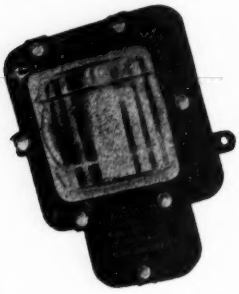

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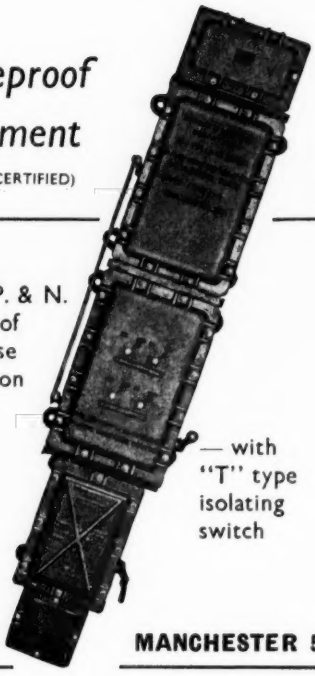

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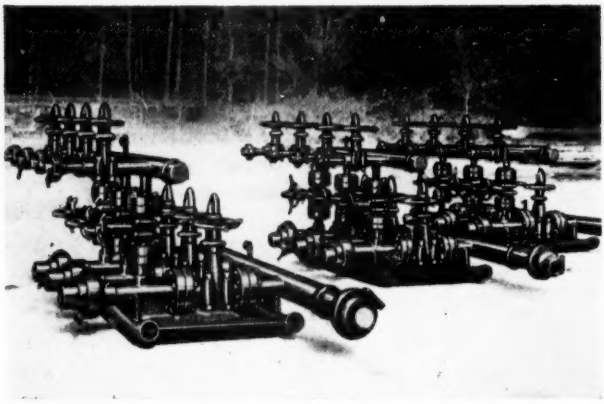

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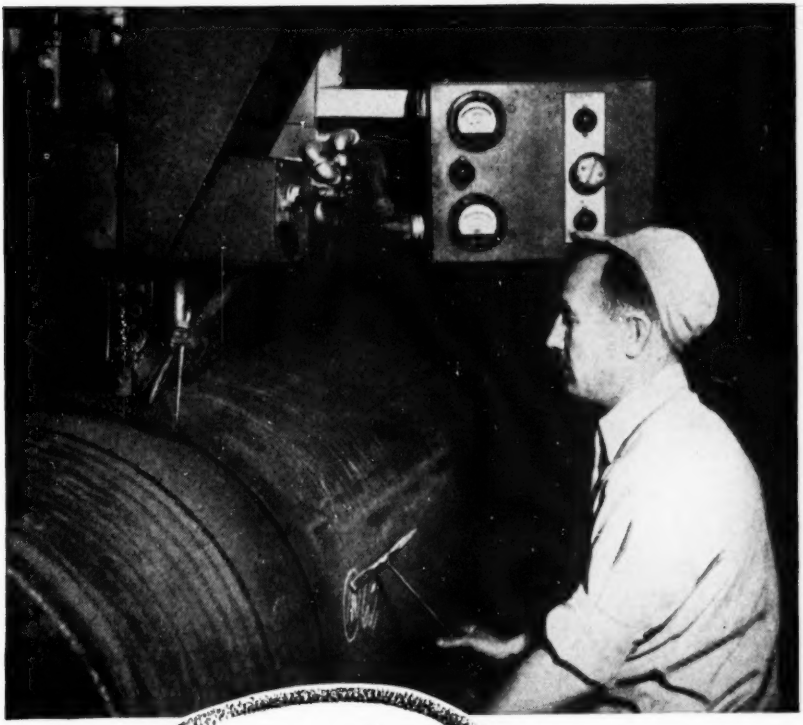

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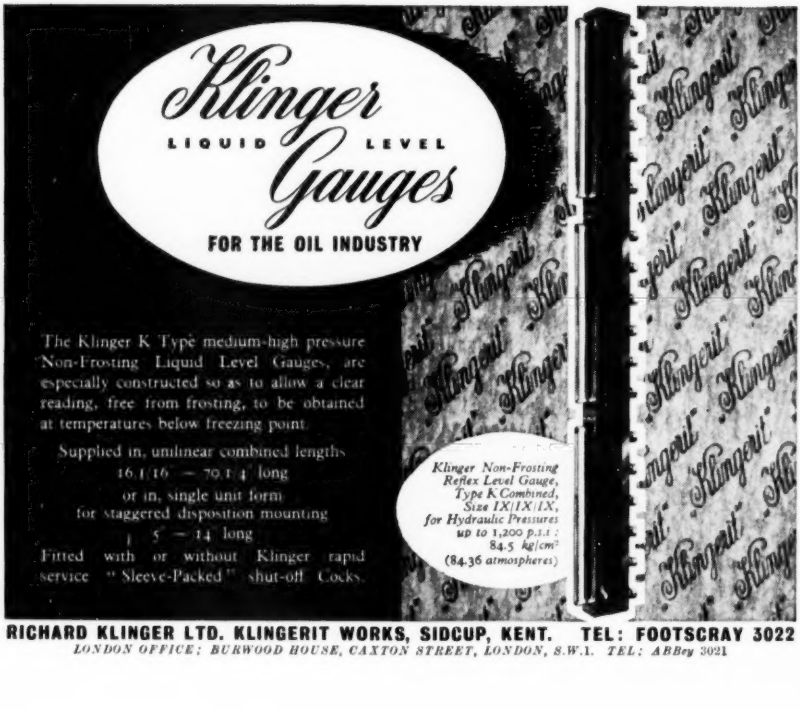
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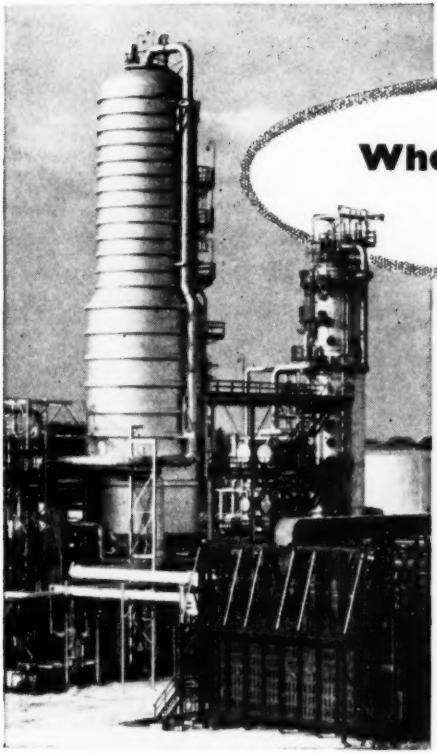

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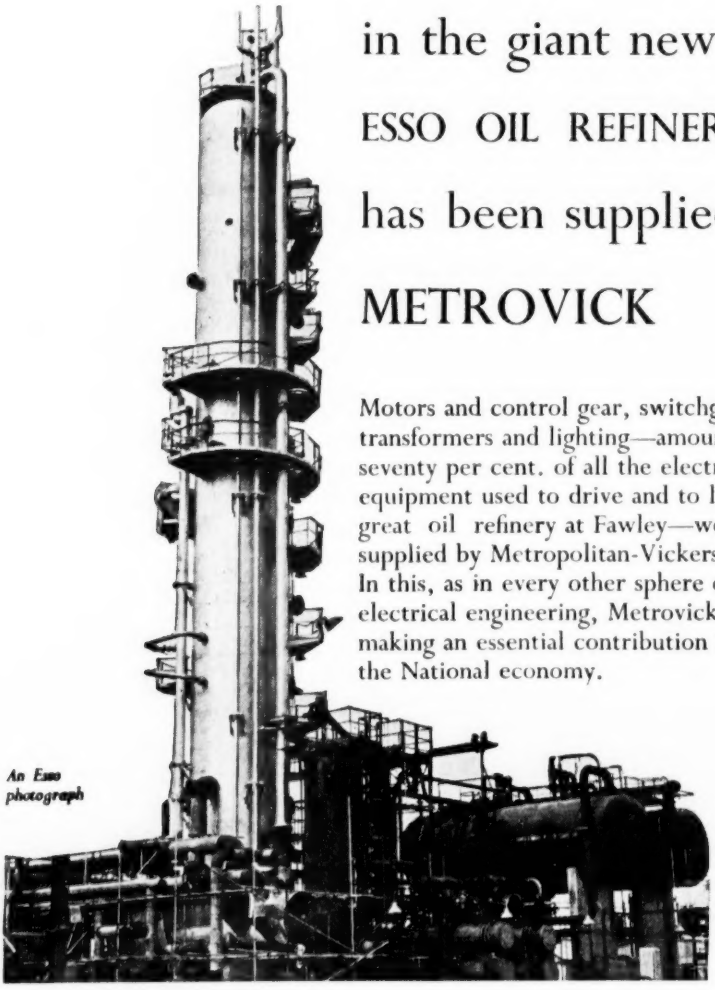

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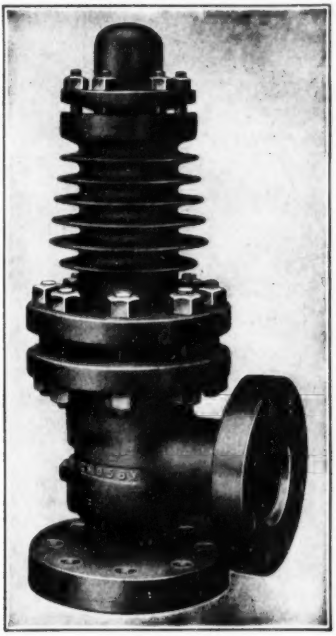

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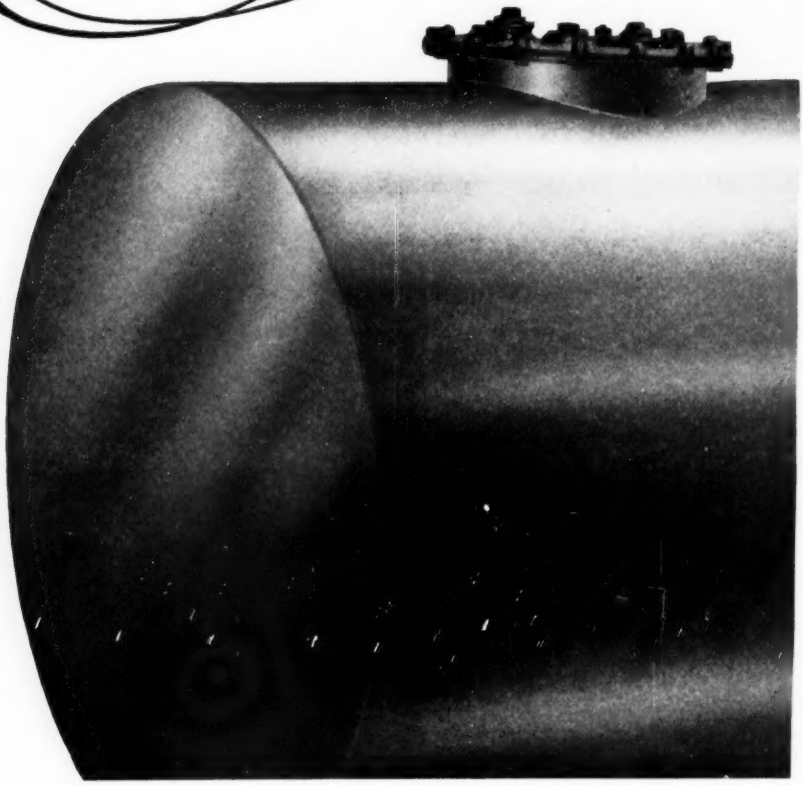

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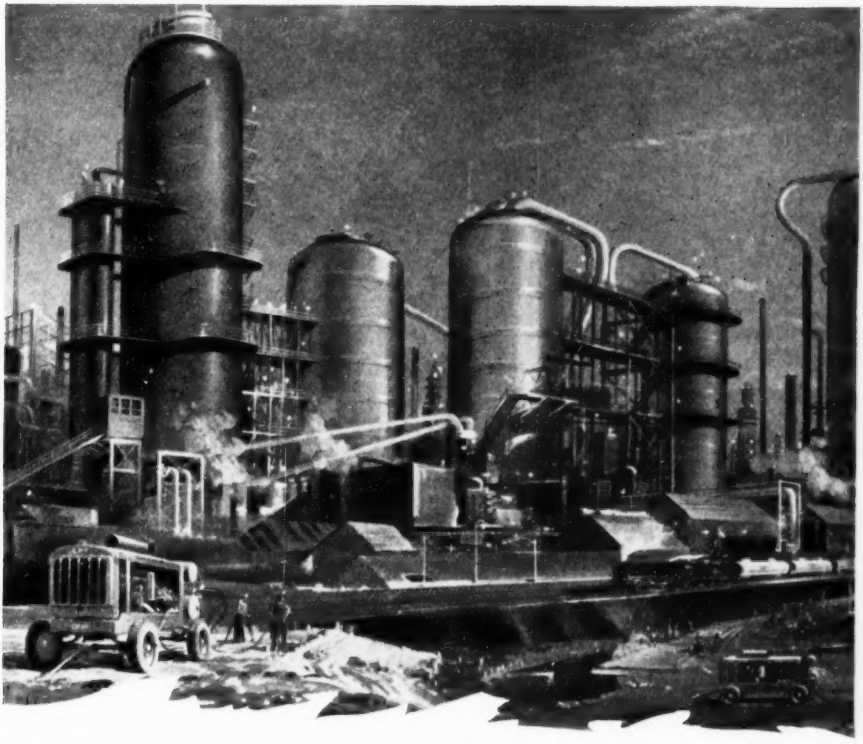

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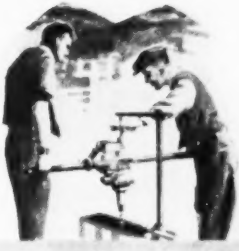

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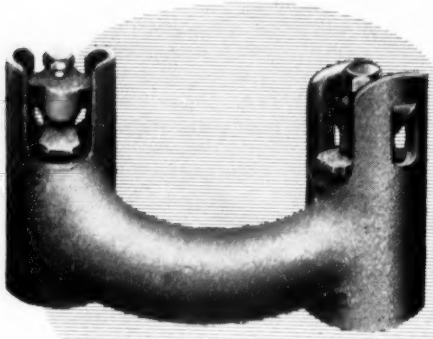

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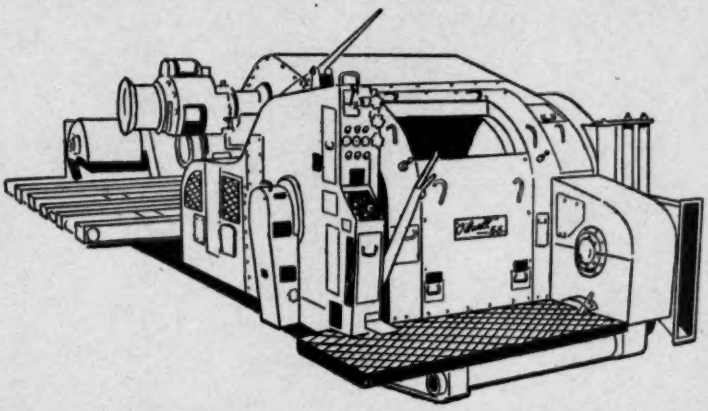

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